THE PRINCIPLES OF CHEMISTRY

BY

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SCIENCE

PRINCIPLES OF CHEMISTRY

(PART FOUR)

CHAPTER XXI

CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM, AND MANGANESE

SULPHUR, selenium, and tellurium belong to the uneven series of the sixth group. In the even series of this group there are known *chromium, molybdenum, tungsten, and uranium*; these give acid oxides of the type RO_3, like SO_3. Their acid properties are less sharply defined than those of sulphur, selenium, and tellurium, as is the case with all elements of the even series as compared with those of the uneven series in the same group. But still the oxides CrO_3, MoO_3, WO_3, and even UO_3, have clearly defined acid properties, and form salts of the composition MO,nRO_3 with bases MO. In the case of the heavy elements, and especially of uranium, the type of oxide, UO_3, is less acid and more basic, because in the even series of oxides the element with the highest atomic weight always acquires a more and more pronounced basic character. Hence UO_3 shows the properties of a base, and gives salts UO_2X_2. The basic properties of chromium, molybdenum, tungsten, and uranium are most clearly expressed in the lower oxides, which they all form. Thus chromic oxide, Cr_2O_3, is as distinct a base as alumina, Al_2O_3.

Of all these elements *chromium* is the most widely distributed and the most frequently used. It gives chromic anhydride, CrO_3, and chromic oxide, Cr_2O_3—two compounds whose relative amounts of oxygen stand in the ratio 2:1. Chromium is, although somewhat rarely, met with in nature as a compound of one or the other type. The red chromium ore of the Urals, lead chromate or crocoisite $PbCrO_4$, was the source in which chromium was discovered by Vauquelin, who gave it this name (from the Greek word signifying colour) owing to the brilliant colours of its compounds; the chromates (salts of chromic anhydride) are red and yellow, and the chromic salts (from Cr_2O_3) green and violet. The red lead chromate is, however, a rare chromium ore found only in the Urals and in a few other localities. Chromic oxide, Cr_2O_3, is more frequently met with. In small quantities it forms the colouring matter of many minerals and rocks—for example, of some serpentines. The commonest ore, and the chief source of the chromium compounds, is the *chrome iron ore* or chromite, which occurs in the Urals[1] and Asia Minor, California, Australia, and other localities. This is magnetic iron ore, FeO,Fe_2O_3, in which the ferric oxide is replaced by chromic oxide, its composition being FeO,Cr_2O_3. Chrome iron ore crystallises in octahedra of sp. gr. 4·4 , it has a feeble metallic lustre, is of a greyish-black colour, and gives a brown powder. It is very feebly acted on by acids, but when fused with potassium acid sulphate it gives a soluble mass, which contains a chromic salt, besides potassium sulphate and ferrous sulphate. In practice the treatment of chrome iron ore is mainly carried on for the preparation of chromates, and not of chromic salts, and therefore we will trace the history of the element by beginning with chromic acid, and especially with the working up of the chrome iron ore into *potassium dichromate*, $K_2Cr_2O_7$, as the most common salt of this acid. It must be remarked that chromic anhydride, CrO_3, is only obtained in an anhydrous state, and is distinguished for its capacity for easily giving anhydro-salts with the alkalis, containing one, two, and even three equivalents of the anhydride to one equivalent of base. Thus among the potassium salts there is known the normal or yellow chromate, K_2CrO_4, which corresponds to, and is perfectly isomorphous with, potassium sulphate, easily forms isomorphous mixtures with it, and is not therefore suitable for a process in which it is necessary to separate the salt from a mixture containing sulphates. As in the presence of a certain excess of acid, the dichromate, $K_2Cr_2O_7 = 2K_2CrO_4 + 2HX - 2KX - H_2O$, is easily formed from K_2CrO_4, the object of the manufacturer is to produce such a dichromate, the more so as it contains a larger proportion of the elements of chromic acid than the normal salt. Finely-ground chrome iron ore, when heated with an alkali, absorbs oxygen almost as easily (Chapter III., Note 7) as a mixture of the oxides of manganese with an alkali. This absorption is due to the presence of chromic oxide, which is oxidised into the anhydride, and then combines with the alkali $Cr_2O_3 + O_3 = 2CrO_3$. As the oxidation and formation of the chromate proceeds, the mass turns *yellow*. The iron is also oxidised, but does not give ferric acid, because the capacity of the chromium for oxidation is incomparably greater than that of the iron.

A mixture of lime (sometimes with potash) and chrome iron ore is heated in a reverberatory furnace, with free access of air and at a red heat for several hours, until the mass becomes yellow; it then contains normal calcium-chromate, $CaCrO_4$, which is insoluble in water in the presence of an excess of lime.[1 bis] The resultant mass is ground up, and treated with water and sulphuric acid. The excess of lime forms gypsum, and the soluble calcium dichromate, $CaCr_2O_7$, together with a certain amount of iron, pass into solution. The solution is poured off, and chalk added to it; this precipitates the ferric oxide (the ferrous oxide is converted into ferric oxide in the furnace) and forms a fresh quantity of gypsum, while the chromic acid remains in solution—that is, it does not form the sparingly-soluble normal salt (1 part soluble in 240 parts of water). The solution then contains a fairly pure calcium dichromate, which by double decomposition gives other chromates; for example, with a solution of potassium sulphate it gives a precipitate of calcium sulphate and a solution of potassium dichromate, which crystallises when evaporated.[2]

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[1] The working of the Ural chrome iron ore into chromium compounds has been firmly established in Russia, thanks to the endeavours of P. K. Ushakoff, who constructed large works for this purpose on the river Kama, near Elabougi, where as much as 2,000 tons of ore are treated yearly, owing to which the importation of chromium preparations into Russia has ceased.

Potassium dichromate, $K_2Cr_2O_7$, easily crystallises from acid solutions in red, well-formed prismatic crystals, which fuse at a red heat and evolve oxygen at a very high temperature, leaving chromic oxide and the normal salt, which undergoes no further change: $2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + O_3$. At the ordinary temperature 100 parts of water dissolve 10 parts of this salt, and the solubility increases as the temperature rises. It is most important to note that the dichromate does not contain water, it is $K_2CrO_4 + CrO_3$, the acid salt corresponding to potassium acid sulphate, $KHSO_4$, does not exist. It does not even evolve heat when dissolving in water, but on the contrary produces cold, *i.e.* it does not form a very stable compound with water. The solution and the salt itself are poisonous, and act as powerful oxidising agents, which is the character of chromic acid in general. When heated with sulphur or organic substances, with sulphurous anhydride, hydrogen sulphide, &c., this salt is deoxidised, yielding chromic compounds.[2 bis] Potassium dichromate[3] is used in the arts and in chemistry as a source for the preparation of all other

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[1 bis] But the calcium chromate is soluble in water in the presence of an excess of chromic acid, as may be seen from the fact that a solution of chromic acid dissolves lime.

[2] There are many variations in the details of the manufacturing processes, and these must be looked for in works on technical chemistry. But we may add that the chromate may also be obtained by slightly roasting briquettes of a mixture of chrome iron and lime, and then leaving the resultant mass to the action of moist air (oxygen is absorbed, and the mass turns yellow).

[2 bis] The oxidising action of potassium dichromate on organic substances at the ordinary temperature is especially marked under the action of light. Thus it acts on gelatin, as Poitevin discovered; this is applied to photography in the processes of photo-

For Note 3 see p. 279.

chromium compounds. It is converted into yellow pigments by means of double decomposition with salts of lead, barium, and zinc. When solutions of the salts of these metals are mixed with potassium dichromate (in dyeing generally mixed with soda, in order to obtain normal salts), they are precipitated as insoluble normal salts; for example, $2BaCl_2 + K_2Cr_2O_7 + H_2O = 2BaCrO_4 + 2KCl + 2HCl$. It follows from this that these salts are insoluble in dilute acids, but the precipitation is not complete (as it would be with the normal salt). The barium and zinc salts are of a lemon yellow colour; the lead salt has a still more intense colour passing into orange. Yellow cotton prints are dyed with this pigment. The silver salt, Ag_2CrO_4, is of a bright red colour.

When potassium dichromate is mixed with potassium hydroxide

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gravure, photo-lithography, pigment printing, &c. Under the action of light this gelatin is oxidised, and the chromic anhydride deoxidised into chromic oxide, which unites with the gelatin and forms a compound insoluble in warm water, whilst where the light has not acted, the gelatin remains soluble, its properties being unaffected by the presence of chromic acid or potassium dichromate.

[5] Ammonium and sodium dichromates are now also prepared on a large scale. The sodium salts may be prepared in exactly the same manner as those of potassium. The normal salt combines with ten equivalents of water, like Glauber's salt, with which it is isomorphous. Its solution above 30° deposits the anhydrous salt. Sodium dichromate crystals contain $Na_2Cr_2O_7,2H_2O$. *The ammonium salts of chromic acid* are obtained by saturating the anhydride itself with ammonia. The dichromate is obtained by saturating one part of the anhydride with ammonia, and then adding a second part of anhydride and evaporating under the receiver of an air-pump. On ignition, the normal and acid salts leave chromic oxide. Potassium ammonium chromate, NH_4KCrO_4, is obtained in yellow needles from a solution of potassium dichromate in aqueous ammonia; it not only loses ammonia and becomes converted into potassium dichromate when ignited, but also by degrees at the ordinary temperature. This shows the feeble energy of chromic acid, and its tendency to form stable dichromates. Magnesium chromate is soluble in water, as also is the strontium salt. The calcium salt is also somewhat soluble, but the barium salt is almost insoluble. The isomorphism with sulphuric acid is shown in the chromates by the fact that the magnesium and ammonium salts form double salts containing six equivalents of water, which are perfectly isomorphous with the corresponding sulphates. The magnesium salt crystallises in large crystals containing seven equivalents of water. The beryllium, cerium, and cobalt salts are insoluble in water. Chromic acid dissolves manganous carbonate, but on evaporation the solution deposits manganese dioxide, formed at the expense of the oxygen of the chromic acid. Chromic acid also oxidises ferrous oxide, and ferric oxide is soluble in chromic acid.

One of the chromates most used by the dyer is the insoluble yellow lead chromate, $PbCrO_4$ (Chapter XVIII., Note 46), which is precipitated on mixing solutions of PbX_2 with soluble chromates. It easily forms a basic salt, having the composition $PbO,PbCrO_4$, as a crystalline powder, obtained by fusing the normal salt with nitre and then rapidly washing in water. The same substance is obtained, although impure and in small quantity, by treating lead chromate with neutral potassium chromate, especially on boiling the mixture; and this gives the possibility of attaining, by means of these materials, various tints of lead chromate, from yellow to red, passing through different orange shades. The decomposition which takes place (incompletely) in this case is as follows: $2PbCrO_4 + K_2CrO_4 = PbCrO_4,PbO + K_2Cr_2O_7$—that is, potassium dichromate is formed in solution.

or carbonate (carbonic anhydride being disengaged in the latter case) it forms the normal salt, K_2CrO_4, known as *yellow chromate of potassium.* Its specific gravity is 2·7, being almost the same as that of the dichromate. It absorbs heat in dissolving; one part of the salt dissolves in 1·75 part of water at the ordinary temperature, forming a yellow solution. When mixed even with such feeble acids as acetic, and more especially with the ordinary acids, it gives the dichromate, and Graham obtained a trichromate, $K_2Cr_3O_{10} = K_2CrO_4,2CrO_3$, by mixing a solution of the latter salt with an excess of nitric acid.

[illegible] anhydride is obtained by preparing a saturated solution of [illegible] at the ordinary temperature, and pouring it in a [illegible] sulphuric acid.[4] On mixing, [illegible] when slowly cooled, the solution [illegible] anhydride in needle-shaped crystals of a red colour [illegible] several centimetres long. The crystals are freed from the mother liquor by placing them on a porous tile.[4 bis] It is very important at this point to call attention to the fact that a hydrate of chromic anhydride is never obtained in the decomposition of chromic compounds, but always the *anhydride*, CrO_3. The corresponding hydrate, CrO_4H_2, or any other hydrate, is not even known. Nevertheless, it must be admitted that chromic acid is bibasic, because it forms salts isomorphous or perfectly analogous with the salts formed by sulphuric acid, which is the best example of a bibasic acid. A clear proof of the bibasicity of CrO_3 is seen in the fact that the anhydride and salts give (when heated with sodium chloride and sulphuric acid) a volatile chloranhydride, CrO_2Cl_2, containing two atoms of chlorine as a bibasic acid should.[5]

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[4] [illegible] nitrogen, because they [illegible] be heated [illegible] hydrochloric acid, oxygen or chlorine [illegible] and a [illegible] is formed. Hence, under these circumstances, [illegible] obtained from its salts. One of the first methods proposed consisted in converting the salts into volatile *chromium hexafluoride*, CrF_6. This compound, obtained by [illegible], may be prepared by mixing lead chromate with [illegible] state and heating the mixture with fuming sulphuric acid in a [illegible] Fuming [illegible] which [illegible] water. It is volatile, and forms a very caustic, [illegible] when [illegible] in a dry platinum vessel into a red, [illegible] in air. The vapours of this [illegible] water [illegible] acid and [illegible] takes the hydro- [illegible] crystals. The [illegible] is also decomposed in the same manner. A solution of chromic acid and a precipitate of barium sulphate are formed by treating the insoluble barium chromate with an equivalent quantity of sulphuric acid. If carefully evaporated, the solution yields crystals of chromic anhydride. Fritzsche gives a very convenient method of preparing chromic anhydride, based on the relation of chromic to sulphuric acid. At the ordinary temperature the strong acid dissolves both chromic anhydride and potassium chromate, but if a certain amount of water is [illegible] the chromic anhydride separates, and if the amount of water be [illegible] the precipitated chromic anhydride is again dissolved. The chromic anhydride [illegible] separated from the mixture when it contains [illegible] equivalents of water [illegible] sulphuric acid. Many methods for the preparation of chromic anhydride are [illegible]

[4 bis] They cannot be dried through paper or washed, because the chromic anhydride is reduced by the filter paper, and is dissolved during the process of washing.

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[5] Berzelius observed, and Rose carefully investigated, this remarkable reaction, which occurs between chromic acid and sodium chloride in the presence of sulphuric acid. If 10 parts of common salt be mixed with 12 parts of potassium dichromate, fused, cooled, and broken up into lumps, and placed in a retort with 20 parts of fuming sulphuric acid, it gives rise to a violent reaction, accompanied by the formation of brown fumes of *chromic chloranhydride*, or *chromyl chloride*, CrO_2Cl_2, according to the reaction: $CrO_3 + 2NaCl + H_2SO_4 = Na_2SO_4 + H_2O + CrO_2Cl_2$. The addition of an excess of sulphuric acid is necessary in order to retain the water. The same substance is always formed when a metallic chloride is heated with chromic acid, or any of its salts, in the presence of sulphuric acid. The formation of this volatile substance is easily observed from the brown colour which is proper to its vapour. On condensing the vapour in a dry receiver a liquid is obtained having a sp. gr. of 1·9, boiling at 118°, and giving a vapour whose density, compared with hydrogen, is 78, which corresponds with the above formula. Chromyl chloride is decomposed by heat into chromic oxide, oxygen, and chlorine: $2CrO_2Cl_2 = Cr_2O_3 + 2Cl_2 + O$; so that it is able to act simultaneously as a powerful oxidising and chlorinating agent, which is taken advantage of in the investigation of many, and especially of organic, substances. When treated with water, this substance first falls to the bottom, and is then decomposed into hydrochloric and chromic acids, like all chloranhydrides: $CrO_2Cl_2 + H_2O = CrO_3 + 2HCl$. When brought into contact with inflammable substances it sets fire to them; it acts thus, for instance, on phosphorus, sulphur, oil of turpentine, ammonia, hydrogen, and other substances. It attracts moisture from the atmosphere with great energy, and must therefore be kept in closed vessels. It dissolves iodine and chlorine, and even forms a solid compound with the latter, which depends upon the faculty of chromium to form its higher oxide, Cr_2O_7. The close analogy in the physical properties of the chloranhydrides, CrO_2Cl_2 and SO_2Cl_2, is very remarkable, although sulphurous anhydride is a gas, and the corresponding oxide, CrO_2, is a non-volatile solid. It may be imagined, therefore, that chromium dioxide (which will be mentioned in the following note) presents a polymerised modification of the substance having the composition CrO_2; in fact, this is obvious from the method of its formation.

If three parts of potassium dichromate be mixed with four parts of strong hydrochloric acid and a small quantity of water, and gently warmed, it all passes into solution, and no chlorine is evolved; on cooling, the liquid deposits red prismatic crystals, known as *Peligot's salt*, very stable in air. This has the composition KCl,CrO_3, and is formed according to the equation $K_2Cr_2O_7 + 2HCl = 2KCl,CrO_3 + H_2O$. It is evident that this is the first chloranhydride of chromic acid, $HCrO_3Cl$, in which the hydrogen is replaced by potassium. It is decomposed by water, and on evaporation the solution yields potassium dichromate and hydrochloric acid. This is a fresh instance of the reversible reactions so frequently encountered. With sulphuric acid Peligot's salt forms chromyl chloride. The latter circumstance, and the fact that Geuther produced Peligot's salt from potassium chromate and chromyl chloride, give reason for thinking that it is a compound of these two substances, $2KCl,CrO_3 = K_2CrO_4 + CrO_2Cl_2$. It is also sometimes regarded as potassium dichromate in which one atom of oxygen is replaced by chlorine—that is, $K_2Cr_2O_6Cl_2$, corresponding with $K_2Cr_2O_7$. When heated it parts with all its chlorine, and on further heating gives chromic oxide.

Chromic anhydride is a red crystalline substance, which is converted into a black mass by heat; it fuses at 190°, and disengages oxygen above 250°, leaving a residue of chromium dioxide, CrO_2,[6] and, on still further heating, chromic oxide, Cr_2O_3. Chromic anhydride is exceedingly soluble in water, and even attracts moisture from the air, but, as was mentioned above, it does not form any definite compound with water. The specific gravity of its crystals is 2·7, and when fused it has a specific gravity 2·6. The solution presents perfectly defined acid properties. It liberates carbonic anhydride from carbonates; gives insoluble precipitates of the chromates with salts of barium, lead, silver, and mercury.

The action of hydrogen peroxide on a solution of chromic acid or of potassium dichromate gives a blue solution, which very quickly becomes colourless with the disengagement of oxygen. Barreswill showed that this is due to the formation of a *perchromic anhydride*, Cr_2O_7, corresponding with sulphur peroxide. This peroxide is remarkable from the fact that it very easily dissolves in ether and is much more stable in this solution, so that, by shaking up hydrogen peroxide mixed with a small quantity of chromic acid, with ether, it is possible to transfer all the blue substance formed to the ether.[6 bis]

With oxygen acids, chromic acid evolves oxygen; for example, with sulphuric acid the following reaction takes place $2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + O_3 + 3H_2O$. It will be readily understood from this that *a mixture of chromic acid* or *of its salts with sulphuric acid* forms an excellent *oxidising agent*, which is frequently employed in chemical laboratories and even for technical purposes as a means of oxidation. Thus hydrogen sulphide and sulphurous anhydride are converted into sulphuric acid by this means. Chromic acid is able to act as a powerful oxidising agent because it passes into chromic oxide, and in so doing disengages half of the oxygen contained in it: $2CrO_3 = Cr_2O_3 + O_3$. Thus chromic anhydride itself is a powerful oxidising agent, and is therefore employed instead of nitric acid in galvanic batteries (as a depolariser), the hydrogen evolved at the carbon being then oxidised, and the chromic acid converted into a non-volatile product of deoxidation, instead of yielding, as nitric acid does, volatile lower oxides of offensive odour. Organic substances are more or less perfectly oxidised by means of chromic anhydride, although this generally requires the aid of heat, and does not proceed in the presence of alkalis, but generally *in the presence of acids*. In acting on a solution of potassium iodide, chromic acid, like many oxidising agents, liberates iodine; the reaction proceeds in proportion to the amount of CrO_3 present, and may serve for determining the amount of CrO_3, since the amount of iodine liberated can be accurately determined by the iodometric method (Chapter XX., Note 42). If chromic anhydride be ignited in a stream of ammonia, it gives chromic oxide, water, and nitrogen. In all cases when chromic acid acts as an oxidising agent in the presence of acids and under the action of heat, the product of its deoxidation is a chromic salt, CrX_3, which is characterised by the green colour of its solution, so that the *red* or yellow *solution* of a salt of chromic acid is then transformed into a *green solution* of a chromic salt, derived from chromic oxide, Cr_2O_3, which is closely analogous to Al_2O_3, Fe_2O_3, and other bases of the composition R_2O_3. This analogy is seen in the insolubility of the anhydrous oxide, in the gelatinous form of the colloidal hydrate, in the formation of alums,[7] of a volatile chloride of chromium, &c.[7 bis]

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[6] This intermediate degree of oxidation, CrO_2, may also be obtained by mixing solutions of chromic salts with solutions of chromates. The brown precipitate formed contains a compound, Cr_2O_3,CrO_3, consisting of equivalent amounts of chromic oxide and anhydride. The brown precipitate of chromium dioxide contains water. The same substance is formed by the imperfect deoxidation of chromic anhydride by various reducing agents. Chromic oxide, when heated, absorbs oxygen, and appears to give the same substance. Chromic nitrate, when ignited, also gives this substance. When this substance is heated it first disengages water and then oxygen, chromic oxide being left. It corresponds with manganese dioxide, $Cr_2O_3,CrO_3 = 3CrO_2$. Krüger treated chromium dioxide with a mixture of sodium chloride and sulphuric acid, and found that chlorine gas was evolved, but that chromyl chloride was not formed. Under the action of light, a solution of chromic acid also deposits the brown dioxide. At the ordinary temperature chromic anhydride leaves a brown stain upon the skin and tissues, which probably proceeds from a decomposition of the same kind. Chromic anhydride is soluble in alcohol containing water, and this solution is decomposed in a similar manner by light. Chromium dioxide forms K_2CrO_4 when treated with H_2O_2 in the presence of KHO.

[6 bis] Now that persulphuric acid $H_2S_2O_8$ is well known it might be supposed that perchromic anhydride, Cr_2O_7, would correspond to perchromic acid, $H_2Cr_2O_8$, but as yet it is not certain whether corresponding salts are formed. Péchard (1891) on adding an excess of H_2O_2 and baryta water to a dilute solution of CrO_3 (8 grm. per litre), observed the formation of a yellow precipitate, but oxygen was disengaged at the same time and the precipitate (which easily exploded when dried) was found to contain, besides an admixture of BaO_2, a compound $BaCrO_5$, and this $= BaO_2 + CrO_3$, and does not correspond to perchromic acid. The fact of its decomposing with an explosion, and the mode of its preparation, proves, however, that this is a similar derivative of peroxide of hydrogen to persulphuric acid (Chapter XX.)

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[7] As a mixture of potassium dichromate and sulphuric acid is usually employed for oxidation, the resultant solution generally contains a double sulphate of potassium and chromium—that is, *chrome alum*, isomorphous with ordinary alum—$K_2Cr_2O_7 + 4H_2SO_4 + 20H_2O = O_3 + K_2Cr_2(SO_4)_4,24H_2O$ or $2(KCr(SO_4)_2,12H_2O)$. It is prepared by dissolving potassium dichromate in dilute sulphuric acid; alcohol is then added and the solution slightly heated, or sulphurous anhydride is passed through it. On the addition of alcohol to a cold mixture of potassium dichromate and sulphuric acid, the gradual disengagement of pleasant-smelling volatile products of the oxidation of alcohol, and especially of aldehyde, C_2H_4O, is remarked. If the temperature of decomposition

For Note 7 bis *see* p. 285.

Chromic oxide, Cr_2O_3, rarely found, and in small quantities, in chrome ochre, is formed by the oxidation of chromium and its lower oxides, by

does not exceed 35°, a *violet* solution of chrome alum is obtained, but if the temperature be higher, a solution of the same alum is obtained of a *green* colour. As chrome alum requires for solution 7 parts of water at the ordinary temperature, it follows that if a somewhat strong solution of potassium dichromate be taken (4 parts of water and 1½ of sulphuric acid to 1 part of dichromate), it will give so concentrated a solution of chrome alum that on cooling, the salt will separate without further evaporation. *If the liquid*, prepared as above or in any instance of the deoxidation of chromic acid, *be heated* (the oxidation naturally proceeds more rapidly) somewhat strongly, for instance, to the boiling-point of water, or if the violet solution already formed be raised to the same temperature, it acquires a bright *green colour*, and on evaporation the same mixture, which at lower temperatures so easily gives cubical crystals of chrome alum, *does not give any crystals whatever* *If the green solution be kept*, however, *for several weeks* at the ordinary temperature, it deposits *violet crystals* of chrome alum. The green solution, when evaporated, gives a non-crystalline mass, and the violet crystals lose water at 100° and turn green. It must be remarked that the transition of the green modification into the violet is accompanied by a decrease in volume (Lecoq de Boisbaudran, Favre). If the green mass formed at the higher temperature be evaporated to dryness and heated at 80° in a current of air, it does not retain more than 6 equivalents of water. Hence Löwel, and also Schrötter, concluded that the green and violet modifications of the alum depend on different degrees of combination with water, which may be likened to the different compounds of sodium sulphate with water and to the different hydrates of ferric oxide.

However, the question in this case is not so simple, as we shall afterwards see. Not chrome alum alone, but *all the chromic salts*, give two, if not three, *varieties*. At least, there is no doubt about the existence of two—a *green* and a *violet modification*. The green chromic salts are obtained by heating solutions of the violet salts, the violet solutions are produced on keeping solutions of the green salts for a long time. The conversion of the violet salts into green by the action of heat is itself an indication of the possibility of explaining the different modifications by their containing different proportions (or states) of water, and, moreover, by the green salts having a less amount of water than the violet. However, there are other explanations. Chromic oxide is a base like alumina, and is therefore able to give both acid and basic salts. It is supposed that the difference between the green and violet salts is due to this fact. This opinion of Krüger is based on the fact that alcohol separates out a salt from the green solution which contains less sulphuric acid than the normal violet salt. On the other hand, Löwel showed that all the acid cannot be separated from the green chromic salts by suitable reagents, as easily as it can be from the same solution of the violet salts; thus barium salts do not precipitate all the sulphuric acid from solutions of the green salts. According to other researches the cause of the variation of the chromic salts lies in a difference in the bases they contain—that is, it is connected with a modification of the properties of the oxide of chromium itself. This only refers to the hydroxides, but as hydroxides themselves are only special forms of salts, the differences observed as yet in this direction between the hydroxides only confirm the generality of the difference observed in the chromic compounds (*see* Note 7 bis).

The salts of chromic oxide, like those of alumina, are easily decomposed, give basic and double salts, and have an acid reaction, as chromic oxide is a feeble base. Potassium and sodium hydroxides give a *precipitate* of the hydroxide with chromic salts, CrX_3. The violet and green salts give a *hydroxide soluble in an excess of the reagent*; but the hydroxide is held in solution by very feeble affinities, so that it is partially separated by heat and dilution with water, and completely so on boiling. In an alkaline solution, chromic hydroxide is easily converted into chromic acid by the action of lead dioxide, chlorine, and other oxidising agents. If the chromic oxide occurs together with such oxides as magnesia, or zinc oxide, then on precipitation the reduction of chromates (for example, of ammonium or mercuric chromate) and by the decomposition (splitting up) of the saline com-

it separates out from its solution in combination with these oxides, forming, for example, ZnO,Cr_2O_3. Viard obtained compounds of Cr_2O_3 with the oxides of Mg, Zn, Cd, &c.) On precipitating the violet solution of chrome alum with ammonia, a precipitate containing $Cr_2O_3,6H_2O$ is obtained, whilst the precipitate from the boiling solution with caustic potash was a hydrate containing four equivalents of water. When fused with borax chromic salts give a green glass. The same coloration is communicated to ordinary glass by the presence of traces of chromic oxide. A chrome glass containing a large amount of chromic oxide may be ground up and used as a green pigment. Among the hydrates of oxide of chromium *Guignet's green* forms one of the widely-used green pigments which have been substituted for the poisonous arsenical copper pigments, such as Schweinfurt green, which formerly was much used. Guignet's green has an extremely bright green colour, and is distinguished for its great stability, not only under the action of light but also towards reagents; thus it is not altered by alkaline solutions, and even nitric acid does not act on it. This pigment remains unchanged up to a temperature of 250°; it contains $Cr_2O_3,2H_2O$, and generally a small amount of alkali. It is prepared by fusing 3 parts of boric acid with 1 part of potassium dichromate; oxygen is disengaged, and a green glass, containing a mixture of the borates of chromium and potassium, is obtained. When cold this glass is ground up and treated with water, which extracts the boric acid and alkali and leaves the above named chromic hydroxide behind. This hydroxide only parts with its water at a red heat, leaving the anhydrous oxide.

The chromic hydroxides lose their water by ignition, and in so doing become spontaneously incandescent, like the ordinary ferric hydroxide (Chapter XXII.). It is not known, however, whether all the modifications of chromic oxide show this phenomenon. The anhydrous *chromic oxide*, Cr_2O_3, is exceedingly difficultly soluble in acids, if it has passed through the above recalescence. But if it has parted with its water, or the greater part of it, and not yet undergone this self-induced incandescence (has not lost a portion of its energy), then it is soluble in acids. It is not reduced by hydrogen. It is easily obtained in various crystalline forms by many methods. The chromates of mercury and ammonium give a very convenient method for its preparation, because when ignited they leave chromic oxide behind. In the first instance oxygen and mercury are disengaged, and in the second case nitrogen and water: $2Hg_2CrO_4 = Cr_2O_3 + O_2 + 4Hg$ or $(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$. The second reaction is very energetic, and the mass of salt burns spontaneously if the temperature be sufficiently high. A mixture of potassium sulphate and chromic oxide is formed by heating potassium dichromate with an equal weight of sulphur: $K_2Cr_2O_7 + S = K_2SO_4 + Cr_2O_3$. The sulphate is easily extracted by water, and there remains a bright green residue of the oxide, whose colour is more brilliant the lower the temperature of the decomposition. The oxide thus obtained is used as a green pigment for china and enamel. The anhydrous chromic oxide obtained from chromyl chloride, CrO_2Cl_2, has a specific gravity of 5·21, and forms almost black crystals, which give a green powder. They are hard enough to scratch glass, and have a metallic lustre. The crystalline form of chromic oxide is identical with that of the oxide of iron and alumina, with which it is isomorphous.

[7 bis] The most important of the compounds corresponding with chromic oxide is *chromic chloride*, Cr_2Cl_6, which is known in an anhydrous and in a hydrated form. It resembles ferric and aluminic chlorides in many respects. There is a great difference between the anhydrous and the hydrated chlorides; the former is insoluble in water, the latter easily dissolves, and on evaporation its solution forms a hygroscopic mass which is very unstable and easily evolves hydrochloric acid when heated with water. The anhydrous form is of a violet colour, and Wöhler gives the following method for its preparation: an intimate mixture is prepared of the anhydrous chromic oxide with carbon and organic matter, and charged into a wide infusible glass or porcelain tube which is heated in a combustion furnace; one extremity of the tube communicates with an apparatus generating chlorine which is passed through several bottles containing sulphuric acid in order

pounds of the oxide itself, CrX_3 or Cr_2X_6, like alumina, which it resembles in forming a feeble base easily giving double and basic salts, which are either green or violet.

to dry it perfectly before it reaches the tube. On heating the portion of the tube in which the mixture is placed and passing chlorine through, a slightly volatile sublimate of chromic chloride, $CrCl_3$ or Cr_2Cl_6, is formed. This substance forms *violet tabular crystals*, which may be distilled in dry chlorine without change, but which, however, require a red heat for their volatilisation. These crystals are greasy to the touch and insoluble in water, but if they be powdered and boiled in water for a long time they pass into *a green solution.* Strong sulphuric acid does not act on the anhydrous salt, or only acts with exceeding slowness, like water. Even aqua regia and other acids do not act on the crystals, and alkalis only show a very feeble action. The specific gravity of the crystals is 2·99. When fused with sodium carbonate and nitre they give sodium chloride and potassium chromate, and when ignited in air they form green chromic oxide and evolve chlorine. On ignition in a stream of ammonia, chromic chloride forms sal-ammoniac and chromium nitride, CrN (analogous to the nitrides BN, AlN). Moberg and Peligot shewed that when chromic chloride is ignited in hydrogen, it parts with one-third of its chlorine, forming chromous chloride, $CrCl_2$—that is, there is formed from a compound corresponding with chromic oxide, Cr_2O_3, a compound answering to the *suboxide*, chromous oxide, CrO—just as hydrogen converts ferric chloride into ferrous chloride with the aid of heat. *Chromous chloride*, $CrCl_2$, forms colourless crystals easily soluble in water, which in dissolving evolve a considerable amount of heat, and form a blue liquid, capable of absorbing oxygen from the air with great facility, being converted thereby into a chromic compound.

The blue solution of chromous chloride may also be obtained by the action of metallic zinc on the green solution of the hydrated chromic chloride; the zinc in this case takes up chlorine just as the hydrogen did. It must be employed in a large excess. Chromic oxide is also formed in the action of zinc on chromic chloride, and if the solution remain for a long time in contact with the zinc the whole of the chromium is converted into chromic oxychloride. Other chromic salts are also reduced by zinc into *chromous salts*, CrX_2, just as the ferric salts FeX_3 are converted into ferrous salts FeX_2 by it. The chromous salts are exceedingly unstable and easily oxidise and pass into chromic salts; hence the reducing power of these salts is very great. From cupric salts they separate cuprous salts, from stannous salts they precipitate metallic tin, they reduce mercuric salts into mercurous and ferric into ferrous salts. Moreover, they absorb oxygen from the air directly. With potassium chromate they give a brown precipitate of chromium dioxide or of chromic oxide, according to the relative amounts of the substances taken: $CrO_3 + CrO = 2CrO_2$ or $CrO_3 + 3CrO = 2Cr_2O_3$. Aqueous ammonia gives a blue precipitate, and in the presence of ammoniacal salts a blue liquid is obtained which turns red in the air from oxidation. This is accompanied by the formation of compounds analogous to those given by cobalt (Chapter XXII.) A solution of chromous chloride with a hot saturated solution of sodium acetate, $C_2H_3NaO_2$, gives, on cooling, transparent red crystals of chromous acetate, $C_4H_6CrO_4,H_2O$. This salt is also a powerful reducing agent, but may be kept for a long time in a vessel full of carbonic anhydride.

The insoluble anhydrous *chromic chloride* $CrCl_3$ very easily *passes into solution* in the presence of a trace (0·004) of *chromous chloride* $CrCl_2$. This remarkable phenomenon was observed by Peligot and explained by Löwel in the following manner: chromous chloride, as a lower stage of oxidation, is capable of absorbing both oxygen and chlorine, combining with various substances. It is able to decompose many chlorides by taking up chlorine from them; thus it precipitates mercurous chloride from a solution of mercuric chloride, and in so doing passes into chromic chloride: $2CrCl_2 + 2HgCl_2 = Cr_2Cl_6 + 2HgCl$. Let us suppose that the same phenomenon takes place when the anhydrous chromic chloride is mixed with a solution of chromous chloride. The latter will then take up a portion of the chlorine of the former, and pass into

The reduction of chromic oxide—for instance, in a solution by zinc and sulphuric acid—leads to the formation of chromous oxide, CrO, and

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soluble hydrate of chromic chloride (hydrochloride of oxide of chromium), and the original anhydrous chromic chloride will pass into chromous chloride. The chromous chloride re-formed in this manner will then act on a fresh quantity of the chromic chloride, and in this manner transfer it entirely into solution as hydrate. This view is confirmed by the fact that other chlorides, capable of absorbing chlorine like chromous chloride, also induce the solution of the insoluble chromic chloride—for example, ferrous chloride, $FeCl_2$, and cuprous chloride. The presence of zinc also aids the solution of chromic chloride, owing to its converting a portion of it into chromous chloride. The solution of chromic chloride in water obtained by these methods is perfectly identical with that which is formed by dissolving chromic hydroxide in hydrochloric acid. On evaporating the *green solution* obtained in this manner, it gives a green mass, containing water. On further heating it leaves a soluble chromic oxychloride, and when ignited it first forms an insoluble oxychloride and then chromic oxide; but no anhydrous chromic chloride, Cr_2Cl_6, is formed by heating the aqueous solution of chromic chloride, which forms an important fact in support of the view that the green solution of chromic chloride is nothing else but hydrochloride of oxide of chromium. At 100° the composition of the green hydrate is $Cr_2Cl_6,9H_2O$, and on evaporation at the ordinary temperature over H_2SO_4 crystals are obtained with 12 equivalents of water; the red mass obtained at 120° contains $Cr_2O_3,4Cr_2Cl_6,24H_2O$. The greater portion of it is soluble in water, like the mass which is formed at 150°. The latter contains $Cr_2O_3,2Cr_2Cl_6,9H_2O = 3(Cr_2OCl_4,3H_2O)$—that is, it presents the same composition as chromic chloride in which one atom of oxygen replaces two of chlorine. And if the hydrate of chromic chloride be regarded as $Cr_2O_3,6HCl$, the substance which is obtained should be regarded as $Cr_2O_3,4HCl$ combined with water, H_2O. The addition of alkalis—for example, baryta—to a solution of chromic chloride immediately produces a precipitate, which, however, re-dissolves on shaking, owing to the formation of one of the oxychlorides just mentioned, which may be regarded as *basic salts*. Thus we may represent the product of the change produced on chromic chloride under the influence of water and heat by the following formulæ: first $Cr_2O_3,6HCl$ or $Cr_2Cl_6,3H_2O$ is formed, then $Cr_2O_3,4HCl,H_2O$ or $Cr_2OCl_4,3H_2O$, and lastly $Cr_2O_3,2HCl,2H_2O$ or $Cr_2O_2Cl_2,3H_2O$. In all three cases there are 2 equivalents of chromium to at least 3 equivalents of water. These compounds may be regarded as being intermediate between chromic hydroxide and chloride; chromic chloride is Cr_2Cl_6, the first oxychloride $Cr_2(OH)_2Cl_4$, the second $Cr_2(OH)_4Cl_2$, and the hydrate $Cr_2(OH)_6$—that is, the chlorine is replaced by hydroxyl.

It is very important to remark two circumstances in respect to this. (1) That the whole of the chlorine in the above compounds is not precipitated from their solutions by silver nitrate; thus the normal salt of the composition $Cr_2Cl_6,9H_2O$ only gives up two-thirds of its chlorine, therefore Péligot supposes that the normal salt contains the oxychloride combined with hydrochloric acid: $Cr_2Cl_6 + 2H_2O = Cr_2O_2Cl_2,4HCl$, and that the chlorine held as hydrochloric acid reacts with the silver, whilst that held in the oxychloride does not enter into reaction, just as we observe a very feebly developed faculty for reaction in the anhydrous chromic chloride; and (2) if the green aqueous solution of $CrCl_3$ be left to stand for some time, it ultimately turns violet; in this form the whole of the chlorine is precipitated by $AgNO_3$, whilst boiling re-converts it into the green variety. Löwel obtained the violet solution of hydrochloride of chromic oxide by decomposing the violet chromic sulphate with barium chloride. Silver nitrate precipitates all the chlorine from this violet modification; but if the violet solution be boiled and so converted into the green modification, silver nitrate then only precipitates a portion of the chlorine.

Recoura (1890–1893) obtained a crystallohydrate of violet chromium sulphate, $Cr_2(SO_4)_3$, with 18 or 15 H_2O. By boiling a solution of this crystallohydrate, he its salts, CrX_2, of a blue colour (*see* Notes 7 and 7 bis). The further

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converted it into the green salt, which, when treated with alkalis, gave a precipitate of $Cr_2O_3,2H_2O$, soluble in $2H_2SO_4$ (and not 3), and only forming the basic salt, $Cr_2(OH)_2(SO_4)_2$. He therefore concludes that the green salts are basic salts. The cryoscopic determinations made by A. Speransky (1892) and Marchetti (1892) give a greater 'depression' for the violet than the green salts, that is, indicate a greater molecular weight for the green salts. But as Étard, by heating the violet sulphate to 100°, converted it into a green salt of the same composition, but with a smaller amount of H_2O, it follows that the formation of a basic salt alone is insufficient to explain the difference between the green and violet varieties, and this is also shown by the fact that $BaCl_2$ precipitates the whole of the sulphuric acid of the violet salt, and only a portion of that of the green salt. A. Speransky also showed that the molecular electro-conductivity of the green solutions is less than that of the violet. It is also known that the passage of the former into the latter is accompanied by an increase of volume, and, according to Recoura, by an evolution of heat also.

Piccini's researches (1894) throw an important light upon the peculiarities of the green chromium trichloride (or chromic chloride); he showed (1) that AgF (in contra-distinction to the other salts of silver) precipitates all the chlorine from an aqueous solution of the green variety; (2) that solutions of green $CrCl_3,6H_2O$ in ethyl alcohol and acetone precipitate all their chlorine when mixed with a similar solution of $AgNO_3$; (3) that the rise of the boiling-point of the ethyl alcohol and acetone green solutions of $CrCl_3,6H_2O$ (Chapter VII., Note 27 bis) shows that i in this case (as in the aqueous solutions of $MgSO_4$ and $HgCl_2$) is nearly equal to 1, that is, that they are like solutions of non-conductors; (4) that a solution of green $CrCl_3$ in methyl alcohol at first precipitates about $\frac{2}{3}$ of its chlorine (an aqueous solution about $\frac{1}{3}$) when treated with $AgNO_3$, but after a time the whole of the chlorine is precipitated; and (5) that an aqueous solution of the green variety gradually passes into the violet, while a methyl alcoholic solution preserves its green colour, both of itself and also after the whole of the chlorine has been precipitated by $AgNO_3$. If, however, in an aqueous or methyl alcholic solution only a portion of the chlorine be precipitated, the solution gradually turns violet. In my opinion the general meaning of all these observations requires further elucidation and explanation, which should be in harmony with the theory of solutions. Recoura, moreover, obtained compounds of the green salt, $Cr_2(SO_4)_3$, with 1, 2, and 3 molecules of H_2SO_4, K_2SO_4, and even a compound $Cr_2(SO_4)_3H_2CrO_4$. By neutralising the sulphuric acid of the compounds of $Cr_2(SO_4)_3$ and H_2SO_4 with caustic soda, Recoura obtained an evolution of 33 thousand calories per each 2NaHO, while free H_2SO_4 only gives 30·8 thousand calories. Recoura is of opinion that special *chromo sulphuric acids*, for instance $(CrSO_4)H_2SO_4 = \frac{1}{2}Cr_2(SO_4)_3H_2SO_4$, are formed. With a still larger excess of sulphuric acid, Recoura obtained salts containing a still greater number of sulphuric acid radicles, but even this method does not explain the difference between the green and violet salts.

These facts must naturally be taken into consideration in order to arrive at any complete decision as to the cause of the different modifications of the chromic salts. We may observe that the green modification of chromic chloride does not give double salts with the metallic chlorides, whilst the violet variety forms compounds $Cr_2Cl_6,2RCl$ (where R = an alkali metal), which are obtained by heating the chromates with an excess of hydrochloric acid and evaporating the solution until it acquires a violet colour. As the result of all the existing researches on the green and violet chromic salts, it appears to me most probable that their difference is determined by the feeble basic character of chromic oxide, by its faculty of giving basic salts, and by the colloidal properties of its hydroxide (these three properties are mutually connected), and moreover, it seems to me that the relation between the green and violet salts of chromic oxide best answers to the relation of the purpureo to the luteo cobaltic salts (Chapter XXII., Note 35). This subject cannot yet be considered as exhausted (*see* Note 7).

We may here observe that with tin the chromic salts, CrX_3, give at low temperatures reduction[8] of oxide of chromium and its corresponding compounds gives *metallic chromium.* Deville obtained it (probably containing carbon) by reducing chromic oxide with carbon, at a temperature near the melting point of platinum, about 1750°, but the metal itself does not fuse at this temperature. Chromium has a steel-grey colour and is very hard (sp. gr. 5·9), takes a good polish, and dissolves in hydrochloric acid, but cold dilute sulphuric and nitric acids have no action upon it. Bunsen obtained metallic chromium by decomposing a solution of chromic chloride, Cr_2Cl_6, by a galvanic current, as scales of a grey colour (sp. gr. 7·3). Wohler obtained crystalline chromium by igniting a mixture of the anhydrous chromic chloride Cr_2Cl_6 (*see* Note 7 bis) with finely-divided zinc, and sodium and potassium chlorides, at the boiling-point of zinc. When the resultant mass has cooled the zinc may

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CrX_2 and SnX_4, whilst at high temperatures, on the contrary, CrX_2 reduces the metal from its salts SnX_2. The reaction, therefore, belongs to the class of reversible reactions (Beketoff).

Poulenc obtained anhydrous CrF_3 (sp. gr. 3·78) and CrF_2 (sp. gr. 4·11) by the action of gaseous HF upon $CrCl_3$. A solution of fluoride of chromium is employed as a mordant in dyeing. Recoura (1890) obtained green and violet varieties of $Cr_2Br_6,6H_2O$. The green variety can only be kept in the presence of an excess of HBr in the solution, if alone its solution easily passes into the violet variety with evolution of heat.

[8] The reduction of metallic chromium proceeds with comparative ease in aqueous solutions. Thus the action of sodium amalgams upon a strong solution of Cr_2Cl_6 gives (first $CrCl_2$) an amalgam of chromium from which the mercury may be easily driven off by heating (in hydrogen to avoid oxidation), and there remains a spongy mass of easily oxidisable chromium. Placet (1891), by passing an electric current through a solution of chrome alum mixed with a small amount of H_2SO_4 and K_2SO_4, obtained hard scales of chromium of a bluish-white colour possessing great hardness and stability (under the action of water, air, and acids). Glatzel (1890) reduced a mixture of $2KCl + Cr_2Cl_6$ by heating it to redness with shavings of magnesium. The metallic chromium thus obtained has the appearance of a fine light-grey powder which is seen to be crystalline under the microscope; its sp. gr. at 16° is 6·7284. It fuses (with anhydrous borax) only at the highest temperatures, and after fusion presents a silver-white fracture. The strongest magnet has no action upon it.

Moissan (1893) obtained chromium by reducing the oxide Cr_2O_3 with carbon in the electrical furnace (Chapter VIII., Note 17) in 9–10 minutes with a current of 350 ampères and 50 volts. The mixture of oxide and carbon gives a bright ingot weighing 100–110 grams. A current of 100 ampères and 50 volts completes the experiment upon a smaller quantity of material in 15 minutes; a current of 30 ampères and 50 volts gave an ingot of 10 grams in 30–40 minutes. The resultant carbon alloy is more or less rich in chromium (from 87·37–91·7 p.c.). To obtain the metal free from carbon, the alloy is broken into large lumps, mixed with oxide of chromium, put into a crucible and covered with a layer of oxide. This mixture is then heated in the electric furnace and the pure metal is obtained. This reduction can also be carried on with chrome iron ore $FeOCr_2O_3$ which occurs in nature. In this case a homogeneous alloy of iron and chromium is obtained If this alloy be thrown in lumps into molten nitre, it forms insoluble sesquioxide of iron and a soluble alkaline chromate. This alloy of iron and chromium dissolved in molten steel (chrome steel) renders it hard and tough, so that such steel has many valuable applications. The alloy, containing about 3 p.c. Cr and about 1·8 p.c. carbon, is even harder than the ordinary kinds of tempered steel and has a fine granular fracture. The usual mode of preparing the ferrochromes for adding to steel is by fusing powdered chrome iron ore under fluxes in a graphite crucible.

be dissolved in dilute nitric acid, and grey crystalline chromium (sp 6·81) is left behind. Frémy also prepared crystalline chromium by action of the vapour of sodium on anhydrous chromic chloride stream of hydrogen, using the apparatus shown in the accompan drawing, and placing the sodium and the chromic chloride in sepa porcelain boats. The tube containing these boats is only heated w it is quite full of dry hydrogen. The crystals of metallic chrom obtained in the tube are grey cubes having a considerable hardness withstanding the action of powerful acids, and even of aqua re The chromium obtained by Wöhler by the action of a galvanic cur is, on the contrary, acted on under these conditions. The reaso this difference must be looked for in the presence of impurities, an the crystalline structure. But in any case, among the propertie

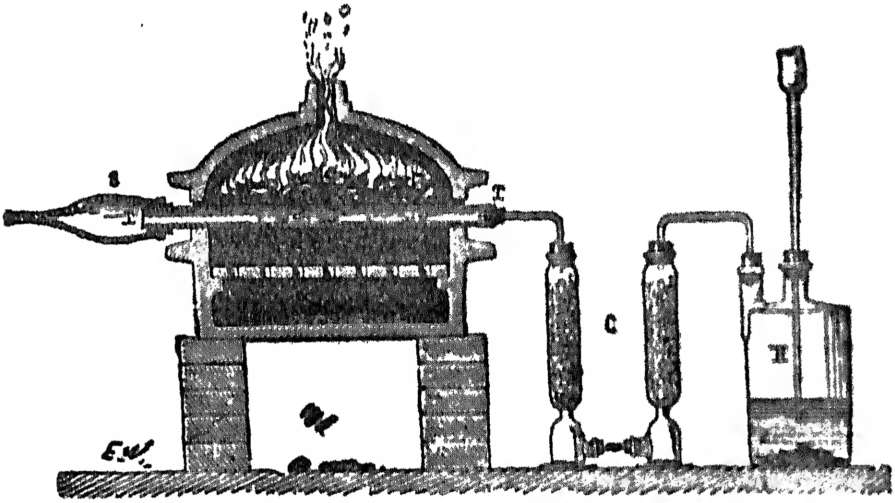

Fig 92.—Apparatus for the preparation of metallic chromium by igniting chromic chlorid and sodium in a stream of hydrogen.

metallic chromium, the following may be considered established : white in colour, with a specific gravity of about 6·7, is extremely h in a crystalline form, is not oxidised by air at the ordinary temperat and with carbon it forms alloys like cast iron and steel.

The two analogues of chromium, *molybdenum* and *tungsten* (or fram), are of still rarer occurrence in nature, and form acid oxides, which are still less energetic than CrO_3. Tungsten occurs in the so what rare minerals, *scheelite*, $CaWO_4$, and *wolfram* ; the latter bein isomorphous mixture of the normal tungstates of iron and mangan in Saxony, Sweden, and Finland. Tungsten ores are sometimes met with in considerable masses in the primary rocks of Bohemia and Saxony, and also in England, America, and the Urals. The preliminary treatment of the ore is very simple; for example, the sulphide, MoS_2, is roasted, and thus converted into sulphurous anhydride and molybdic anhydride, MoO_3, which is then dissolved in alkalis, generally in ammonia. The ammonium molybdate is then treated with acids, when the sparingly soluble molybdic acid is precipitated. Wolfram is treated in a different manner. Most frequently the finely-ground ore is repeatedly boiled with hydrochloric and nitric acids, and the resultant solutions (of salts of manganese and iron) poured off, until the dark brown mass of ore disappears, whilst the tungstic acid remains, mixed with silica, as an insoluble residue; it is treated also with ammonia, and is thus converted into soluble ammonium tungstate, which passes into solution and yields tungstic acid when treated with acids. This hydrate is then ignited, and leaves tungstic anhydride. The general character of molybdic and tungstic anhydrides is analogous to that of chromic anhydride; they are anhydrides of a feebly acid character, which easily give polyacid salts and colloid solutions.[8 bis]

[8 bis] The atomic composition of the tungsten and molybdenum compounds is taken as being identical with that of the compounds of sulphur and chromium, because (1) both these metals give two oxides in which the amounts of oxygen per given amount of metal stand in the ratio 2 : 3, (2) the higher oxide is of the latter kind, and, like chromic and sulphuric anhydrides, it has an acid character, (3) certain of the molybdates are isomorphous with the sulphates; (4) the specific heat of tungsten is 0.0334, consequently the product of the atomic weight and specific heat is 6.15, like that of the other elements—it is the same with molybdenum, $96.0 \times 0.0722 = 6.9$, (5) tungsten forms with chlorine not only compounds WCl_6, WCl_5, and $WOCl_4$, but also WO_2Cl_2, a volatile substance the analogue of chromyl chloride, CrO_2Cl_2, and sulphuryl chloride, SO_2Cl_2. Molybdenum gives the chlorine compounds, $MoCl_2$, $MoCl_3$(?), $MoCl_4$ (fuses at 194°, boils at 268°; according to Debray it contains $MoCl_5$), $MoOCl_4$, MoO_2Cl_2, and $MoO_2(OH)Cl$. The existence of tungsten hexachloride, WCl_6, is an excellent proof of the fact that the type SX_6 appears in the analogues of sulphur as in SO_3; (6) the vapour density accurately determined for the chlorine compounds $MoCl_4$, WCl_6, WCl_5, $WOCl_4$ (Roscoe) leaves no doubt as to the molecular composition of the compounds of tungsten and molybdenum, for the observed and calculated results entirely agree.

Tungsten is sometimes called scheele in honour of Scheele, who discovered it in 1781 and molybdenum in 1778. Tungsten is also known as wolfram; the former name was the name given to it by Scheele, because he extracted it from the mineral then known as tungsten and now called scheelite, $CaWO_4$. The researches of Roscoe, Blomstrand and others have subsequently thrown considerable light on the whole history of the compounds of molybdenum and tungsten.

The ammonium salts of tungsten and molybdic acids when ignited leave the anhy-

Hydrogen (which does not directly form compounds with Cr, Mo,

4·4; whilst on further heating in open vessels or in a stream of air this anhydride *sublimes* in pearly scales—this enables it to be obtained in a tolerably pure state. Water dissolves it in small quantities—namely, 1 part requires 600 parts of water for its solution. The hydrates of molybdic anhydride are *soluble also in acids* (a hydrate, H_2MoO_4, is obtained from the nitric acid solution of the ammonium salt), which forms one of their distinctions from the tungstic acids. But after ignition molybdic anhydride is insoluble in acids, like tungstic anhydride; alkalis dissolve this anhydride, easily forming molybdates. Potassium bitartrate dissolves the anhydride with the aid of heat. None of the acids yet considered by us form so many different salts with one and the same base (alkali) as molybdic and tungstic acids. The composition of these salts, and their properties also, vary considerably. The most important discovery in this respect was made by Marguerite and Laurent, who showed that the salts which contain a large proportion of tungstic acid are easily soluble in water, and ascribed this property to the fact that tungstic acid may be obtained *in several states.* The common tungstates, obtained with an excess of alkali, have an alkaline reaction, and on the addition of sulphuric or hydrochloric acid first deposit an acid salt and then a hydrate of tungstic acid, which is insoluble both in water and acids; but if instead of sulphuric or hydrochloric acids, we add acetic or phosphoric acid, or if the tungstate be saturated with a fresh quantity of tungstic acid, which may be done by boiling the solution of the alkali salt with the precipitated tungstic acid, a solution is obtained which, on the addition of sulphuric or a similar acid, does not give a precipitate of tungstic acid at the ordinary or at higher temperatures. The solution then contains peculiar salts of tungstic acid, and if there be an excess of acid it also contains tungstic acid itself; Laurent, Riche, and others called it *metatungstic acid,* and it is still known by this name. Those salts which with acids immediately give the insoluble tungstic acid have the composition R_2WO_4, $RHWO_4$, whilst those which give the soluble metatungstic acid contain a far greater proportion of the acid elements. Scheibler obtained the (soluble) metatungstic acid itself by treating the soluble barium (meta) tetratungstate, $BaO,4WO_3$, with sulphuric acid. Subsequent research showed the existence of a similar phenomenon for molybdic acid. There is no doubt that this is a case of colloidal modifications.

Many chemists have worked on the various salts formed by molybdic and tungstic acids. The tungstates have been investigated by Marguerite, Laurent, Marignac, Riche, Scheibler, Anthon, and others. The molybdates were partially studied by the same chemists, but chiefly by Struve and Svanberg, Delafontaine, and others. It appears that for a given amount of base the salts contain one to eight equivalents of molybdic or tungstic anhydride; *i.e.* if the base have the composition RO, then the highest proportion of base will be contained by the salts of the composition $ROWO_3$ or $ROMoO_3$—that is, by those salts which correspond with the normal acids H_2WO_4 and H_2MoO_4, of the same nature as sulphuric acid; but there also exist salts of the composition $RO,2WO_3$, $RO,3WO_3$ $RO,8WO_3$. The water contained in the composition of many of the acid salts is often not taken into account in the above. The properties of the salts holding different proportions of acids vary considerably, but one salt may be converted into another by the addition of acid or base with great facility, and the greater the proportion of the elements of the acid in a salt, the more stable, within a certain limit, is its solution and the salt itself.

The most common ammonium molybdate has the composition $(NH_4HO)_6,H_2O,7MoO_3$ (or, according to Marignac and others, NH_4HMoO_4), and is prepared by evaporating an ammoniacal solution of molybdic acid. It is used in the laboratory for precipitating phosphoric acid, and is purified for this purpose by mixing its solution with a small quantity of magnesium nitrate, in order to precipitate any phosphoric acid present, filtering, and then adding nitric acid and evaporating to dryness. A pure ammonium molybdate free from phosphoric acid may then be extracted from the residue.

Phosphoric acid forms insoluble compounds with the oxides of uranium and iron, tin, bismuth, &c., having feeble basic and even acid properties. This perhaps depends

on the fact that the atoms of hydrogen in phosphoric acid are of a very
character, as we saw above. Those atoms of hydrogen which are replaced with
by ammonium, sodium, &c., are probably easily replaced by feebly energe
groups—that is, the formation of particular complex substances may be exp
take place at the expense of these atoms of the hydrogen of phosphoric acid
certain feeble metallic acids; and these substances will still be acids, bec
hydrogen of the phosphoric acids and metallic acids, which is easily replaced by
is not removed by their mutual combination, but remains in the resultant co
Such a conclusion is verified in the *phosphomolybdic acids* obtained (1888) by
If a solution of ammonium molybdate be acidified, and a small amount of a solu
may be acid) containing orthophosphoric acid or its salts be added to it (so that t
at least 40 parts of molybdic acid present to 1 part of phosphoric acid), then after
of twenty-four hours the whole of the phosphoric acid is separated as a yellow pre
containing, however, not more than 3 to 4 p.c. of phosphoric anhydride, about
ammonia, about 90 p.c. of molybdic anhydride, and about 4 p.c. of water. The fo
of this precipitate is so distinct and so complete that this method is employed for
covery and separation of the smallest quantities of phosphoric acid. Phosphoric
found to be present in the majority of rocks by this means. The precipitate is
in ammonia and its salts, in alkalis and phosphates, but is perfectly insoluble
sulphuric, and hydrochloric acids in the presence of ammonium molybdate. The
sition of the precipitate appears to vary under the conditions of its precipitation
nature became clear when the acid corresponding with it was obtained. If the
described yellow precipitate be boiled in aqua regia, the ammonia is destroy
an acid is obtained in solution, which, when evaporated in the air, crystallises out
oblique prisms of approximately the composition $P_2O_5,20MoO_3,26H_2O$ Such an
proportion of component parts is explained by the above-mentioned consideratio
saw above that molybdic acid easily gives salts $R_2OnMoO_3mH_2O$, which we may
to correspond to a hydrate $MoO_2(HO)_2nMoO_3mH_2O$. And suppose that such a
reacts on orthophosphoric acid, forming water and compounds of the com
$MoO_2(HPO_4)nMoO_3mH_2O$ or $MoO_2(H_2PO_4)_2nMoO_3mH_2O$; this is actually the
tion of phosphomolybdic acid. Probably it contains a portion of the hydrogen rep
by metals of both the acids H_3PO_4 and of H_2MoO_4. The crystalline acid
probably $H_3MoPO_7,9MoO_3,12H_2O$. This acid is really tribasic, because its
solution precipitates salts of potassium, ammonium, rubidium (but not lithi
sodium) *from acid solutions*, and gives a *yellow* precipitate of the com
$R_3MoPO_7,9MoO_3,8H_2O$, where R = NH_4. Besides these, salts of another com
may be obtained, as would be expected from the preceding. These salts are only
in acid solutions (which is naturally due to their containing an excess of acid
whilst under the action of alkalis they give *colourless* phosphomolybdates of the
sition $R_3MoPO_5,MoO_4,8H_2O$. The corresponding salts of potassium, silver, amm
are easily soluble in water and crystalline.

Phosphomolybdic acid is an example of the *complex inorganic acids* first
by Marignac and afterwards generalised and studied in detail by Gibbs. W
afterwards meet with several examples of such acids, and we will now turn atte
the fact that they are usually formed by weak polybasic acids (boric, silicic, m
&c.), and in certain respects resemble the cobaltic and such similar complex com
with which we shall become acquainted in the following chapter. As an example
here mention certain complex compounds containing molybdic and tungstic acids,
will illustrate the possibility of a considerable complexity in the composition
The action of ammonium molybdate upon a dilute solution of purpureo-cobaltic
Chapter XXII.) acidulated with acetic acid gives a salt which after drying at 100°
composition $Co_2O_310NH_37MoO_38H_2O$. After ignition this salt leaves a residue hav
composition $2CoO7MoO_3$. An analogous compound is also obtained for tungstic acid,
the composition $Co_2O_310NH_310WO_39H_2O$. In this case after ignition there remain

this forms the means of obtaining metallic molybdenum

of the composition $CoO5WO_3$ (Carnot, 1889). Professor Kournakoff, by tre
potassium and sodium molybdates, containing a certain amount of subox
bromine obtained salts having the composition: $3K_2OCo_2O_312MoO_320$
and $3K_2OCo_2O_310Mo_310H_2O$ (dark green). Péchard (1893) obtained salts o
phosphotungstic acids by evaporating equivalent mixtures of solutions o
and metatungstic acid (*see* further on): phosphotrimetatungstic acid P
phosphotetrametatungstic acid $P_2O_516WO_369H_2O$, phosphopentam
$P_2O_520WO_3H_2O$, and phosphohexametatungstic acid $P_2O_524WO_359H$
and Frankel described still more complex salts, such as: $3Ag_2O4BaO$
$5BaO2K_2OP_2O_522WO_348H_2O$. Analogous double salts with $22WO_3$ we
with KSr, KHg, BaHg, and NH_4Pb. Kehrmann (1892) considers
obtaining an unlimited number of such salts to be a general character
pounds. Mahon and Friedheim (1893) obtained compounds of simila
molybdic and arsenic acids.

For tungstic acid there are known: (1) Normal salts—for example,
so-called acid salts have a composition like $3K_2O,7WO_3,6H_2O$ or K_6H_6(
the tritungstates like $Na_2O,3WO_3,3H_2O = Na_2H_4(WO_4)_3,H_2O$. All thes
salts are soluble in water, but are precipitated by barium chloride, and
tion give an insoluble hydrate of tungstic acid; whilst those salts which
below do not give a precipitate either with acids or with the salts of the
cause they form soluble salts even with barium and lead. They are gene
tungstates. They all contain water and a larger proportion of acid e
preceding salts; (4) the tetratungstates, like $Na_2O,4WO_3,10H_2O$ and Ba
example; (5) the octatungstates—for example, $Na_2O,8WO_3,24H_2O$. Sa
states lose so much water at 100° that they leave salts whose compos
with an acid, $3H_2O,4WO_3$—that is, $H_6W_4O_{15}$—whilst in the meta salts
are replaced by metals, it is assumed, although without much ground
contain a particular soluble metatungstic acid of the composition H_6W

As an example we will give a short description of the sodium sa
salt, Na_2WO_4, is obtained by heating a strong solution of sodium carbon
acid to a temperature of 80°; if the solution be filtered hot, it crysta
tabular crystals, having the composition $Na_2WO_4,2H_2O$, which remain
air and are easily soluble in water. When this salt is fused with a
tungstic acid, it gives a ditungstate, which is soluble in water and s
solution in crystals containing water. The same salt is obtained by
hydrochloric acid to the solution of the normal salt so long as a pre
appear, and the liquid still has an alkaline reaction. This salt was
have the composition $Na_2W_2O_7,4H_2O$, but it has since been found to
$Na_6W_7O_{24},16H_2O$—that is, it corresponds with the similar salt of m lyb

(If this salt be heated to a red heat in a stream of hydrogen, it loses
oxygen, acquires a metallic lustre, and turns a golden yellow colour,
treated with water, alkali, and acid, leaves golden yellow leaflets and
very like gold. This very remarkable substance, discovered by Wöhle
to Malaguti's analysis, the composition $Na_2W_3O_9$; that is, it, as it
double tungstate of tungsten oxide, WO_2, and of sodium, Na_2WO_4
decomposition of the fused sodium salt is best effected by finely divide
stance has a sp. gr. 6·6; it conducts electricity like metals, and like the

Both metals are infusible, and both under the action of heat form

anhydrous, sparingly soluble tetratungstate, $Na_2WO_4,3WO_3$, which, when heated at 120° in a closed tube with water, passes into an easily soluble metatungstate. It may therefore be said that the metatungstates are hydrated compounds. On boiling a solution of the above-mentioned salts of sodium with the yellow hydrate of tungstic acid they give a solution of metatungstate, which is the hydrated tetratungstate. Its crystals contain $Na_2W_4O_{13},10H_2O$. After the hydrate of tungstic acid (obtained from the ordinary tungstates by precipitation with an acid) has stood a long time in contact with a solution (hot or cold) of sodium tungstate, it gives a solution which is not precipitated by hydrochloric acid; this must be filtered and evaporated over sulphuric acid in a desiccator (it is decomposed by boiling). It first forms a very dense solution (aluminium floats in it) of sp. gr. 3·0, and octahedral crystals of *sodium metatungstate*, $Na_2W_4O_{13},10H_2O$, sp. gr. 3·85, then separate. It effloresces and loses water, and at 100° only two out of the ten equivalents of water remain, but the properties of the salt remain unaltered. If the salt be deprived of water by further heating, it becomes insoluble. At the ordinary temperature one part of water dissolves ten parts of the metatungstate. The other metatungstates are easily obtained from this salt. Thus a strong and hot solution, mixed with a like solution of barium chloride, gives on cooling crystals of barium metatungstate, $BaW_4O_{13},9H_2O$. These crystals are dissolved without change in water containing hydrochloric acid, and also in hot water, but they are partially decomposed by cold water, with the formation of a solution of metatungstic acid and of the normal barium salt $BaWO_4$.

In order to explain the difference in the properties of the salts of tungstic acid, we may add that a mixture of a solution of tungstic acid with a solution of silicic acid does not coagulate when heated, although the silicic acid alone would do so; this is due to the formation of a silicotungstic acid, discovered by Marignac, which presents a fresh example of a complex acid. A solution of a tungstate dissolves gelatinous silica, just as it does gelatinous tungstic acid, and when evaporated deposits a crystalline salt of silicotungstic acid. This solution is not precipitated either by acids (a clear analogy to the metatungstates) or by sulphuretted hydrogen, and corresponds with a series of salts. These salts contain one equivalent of silica and 8 equivalents of hydrogen or metals, in the same form as in salts, to 12 or 10 equivalents of tungstic anhydride; for example, the crystalline potassium salt has the composition $K_8W_{12}SiO_{42},14H_2O = 4K_2O,12WO_3,SiO_2,14H_2O$. Acid salts are also known in which half of the metal is replaced by hydrogen. The complexity of the composition of such complex acids (for example, of the phosphomolybdic acid) involuntarily leads to the idea of polymerisation, which we were obliged to recognise for silica, lead oxide, and other compounds. This polymerisation, it seems to me, may be understood thus: a hydrate A (for example, tungstic acid) is capable of combining with a hydrate B (for example, silica or phosphoric acid, with or without the disengagement of water), and by reason of this faculty it is capable of polymerisation—that is, A combines with A—combines with itself—just as aldehyde, C_2H_4O, or the cyanogen compounds are able to combine with hydrogen, oxygen, &c., and are liable to polymerisation. On this view the molecule of tungstic acid is probably much more complex than we represent it; this agrees with the easy volatility of such compounds as the chloranhydrides, CrO_2Cl_2, MoO_2Cl_2, the analogues of the volatile sulphuryl chloride, SO_2Cl_2, and with the non-volatility, or difficult volatility, of chromic and molybdic anhydrides, the analogues of the volatile sulphuric anhydride. Such a view also finds a certain confirmation in the researches made by Graham on the colloidal

renders the latter ductile and hard).[9] Molybdenum forms a grey pov
which scarcely aggregates under a most powerful heat, and has a sp
gravity of 8·5 It is not acted on by the air at the ordinary tem
ture, but when ignited it is first converted into a brown, and then i
blue oxide, and lastly into molybdic anhydride. Acids do not act
—that is, it does not liberate hydrogen from them, not even
hydrochloric acid—but strong sulphuric acid disengages sulphu
anhydride, forming a brown mass, containing a lower oxide of m
denum. Alkalis in solution do not act on molybdenum, but when

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has a bitter, astringent taste, and does not yield gelatinous tungstic acid (hyd
either when heated or on the addition of acids or salts. It may also be evaporat
dryness; it then forms a vitreous mass of the *hydxosol of tungstic acid*, which ad
strongly to the walls of the vessel in which it has been evaporated, and is per
soluble in water. It does not even lose its solubility after having been heated to
and only becomes insoluble when heated to a red heat, when it loses about 2½ p
water. The dry acid, dissolved in a small quantity of water, forms a gluey mas
like gum arabic, which is one of the representatives of the hydrosols of col
substances. The solution, containing 5 p.c of the anhydride, has a sp. gr. of 1·047
20 p.c., of 1·217; with 50 p.c., of 1·80; and with 80 p.c., of 3·24. The presence
polymerised trioxide in the form of hydrate, $H_2OW_3O_9$ or H_2O4WO_3, must th
recognised in the solution: this is confirmed by Sabanoeff's cryoscopic determin
(1889). A similar stable solution of molybdic acid is obtained by the dialysis
mixture of a strong solution of sodium molybdate with hydrochloric acid (the preci
which is formed is re-dissolved). If $MoCl_4$ be precipitated by ammonia and washe
water, a point is reached at which perfect solution takes place, and the molybdi
forms a colloid solution which is precipitated by the addition of ammonia (Muthn
The addition of alkali to the solutions of the hydrosols of tungstic and molybdic
immediately results in the re-formation of the ordinary tungstates and molyb
There appears to be no doubt but that the same transformation is accomplished
passage of the ordinary tungstates into the metatungstates as takes place in the p
of tungstic acid itself from an insoluble into a soluble state; but this may be
actually proved to be the case, because Scheibler obtained a solution of tungstic
before Graham, by decomposing barium metatungstate ($BaO4WO_3,9H_2O$) with sul
acid. By treating this salt with sulphuric acid in the amount required for the p
tation of the baryta, Scheibler obtained a solution of metatungstic acid which,
containing 43·75 p.c. of acid, had a sp. gr. of 1·634, and with 27·61 p.c. a sp. gr. of 1
that is, specific gravities corresponding with those found by Graham.

Péchard found that as much heat is evolved by neutralising metatungstic acid a
sulphuric acid.

Questions connected with the metamorphoses or modifications of tungsti
molybdic acids, and the polymerisation and colloidal state of substances, as well
formation of complex acids, belong to that class of problems the solution of
will do much towards attaining a true comprehension of the mechanism of a num
chemical reactions. I think, moreover, that questions of this kind stand in intimat
nection with the theory of the formation of solutions and alloys and other so-called
finite compounds.

[9] Moissan (1893) studied the compounds of Mo and W formed with carbon
electrical furnace (they are extremely hard) from a mixture of the anhydrides and c
Poleck and Grützner obtained definite compounds FeW_2 and FeW_2C_3 for tun
Metallic W and Mo displace Ag from its solutions but not Pb. There is reason for beli
that the sp. gr. of pure molybdenum is higher than that (8·5) generally ascribed

with it hydrogen is given off, which shows, as does its whole ch
the acid properties of the metal. The properties of tungsten ar
identical ; it is infusible, has an iron-grey colour, is exceedingly
that it even scratches glass. Its specific gravity is 19·1 (acco
Roscoe), so that, like uranium, platinum, &c., it is one of the
metals.[9 bis] Just as sulphur and chromium have their corres
persulphuric and perchromic acids, $H_2S_2O_8$ and H_2CrO_8, hav
properties of peroxides, and corresponding to peroxide of hydr
also molybdenum and tungsten are known to give *permolybdic*
tungstic acids, $H_2Mo_2O_8$ and $H_2W_2O_8$, which have the propertie
peroxides, *i.e.* easily disengage iodine from KI and chlorine fro
easily part with their oxygen, and are formed by the action of
of hydrogen, into which they are readily reconverted (hence th
be regarded as compounds of H_2O_2 with $2MoO_3$ and $2WO_3$), &c.
formation (Baerwald 1884, Kemmerer 1891) is at once seen
coloration (not destroyed by boiling), which is obtained on m
solution of the salts with peroxide of hydrogen, and on treating
stance, molybdic acid with a solution of peroxide of hydrogen (
1892). The acid then forms an orange-coloured solution, whi
evaporation in vacuo leaves $Mo_2H_2O_8 4H_2O$ as a crystalline
and loses $4H_2O$ at 100°, beyond which it decomposes with the
tion of oxygen.[9 tri]

Uranium, U=240, has the highest atomic weight of
analogues of chromium, and indeed of all the elements yet know

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[9 bis] We may conclude our description of tungsten and molybdenum by st
their sulphur compounds have an acid character, like carbon bisulphide or st
phide. If sulphuretted hydrogen be passed through a solution of a molybd
not give a precipitate unless sulphuric acid be present, when a dark brown pro
molybdenum trisulphide, MoS_3, is formed. When this sulphide is ignited with
of air it gives the bisulphide MoS_2; the latter is not able to combine with potassium
like the trisulphide MoS_3, which forms a salt, K_2MoS_4, corresponding with
This is soluble in water, and separates out from its solution in red crystals, whi
metallic lustre and reflect a green light. It is easily obtained by heating t
bisulphide, MoS_2, with potash, sulphur, and a small amount of charcoal, which
deoxidising the oxygen compounds. Tungsten gives similar compounds, R_2W
R = NH_4, K, Na. They are decomposed by acids, with the separation of tungs
phide, WS_3, and molybdenum trisulphide, MoS_3. Rideal (1892) obtained W_2N_3 b
WO_3 in NH_3. This compound exhibited the general properties of metallic nit

[9 tri] When peroxide of hydrogen acts upon a solution of potassium molyb
formed yellow crystals belonging to the triclinic system separate out in the col
these crystals are heated in vacuo they first lose water and then decompose

Although it gives sparingly-soluble yellow compounds with alk
which fully correspond with the dichromates—for example, Na_2U
$=Na_2O,2UO_3$,[10]—yet it more frequently and easily reacts with acids, I

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solution of peroxide of hydrogen for several minutes. The solution rapidly turns y
and no longer gives a precipitate of tungstic anhydride when treated with nitric
When evaporated in vacuo the solution leaves a thick syrupy liquid from which ray
crystals separate out; these crystals are more soluble in water than the salt origi
taken. When heated they also lose water and oxygen. Their composition answe
the formula $M_2W_2O_8 2H_2O$, where M = Na, NH_4, &c. The permolybdates and
tungstates have similar properties. When treated with oxygen acids they give per
of hydrogen, and disengage chlorine and iodine from hydrochloric acid and pota
iodide.

Piccini (1891) showed that peroxide of hydrogen not only combines with the ox
compounds of Mo and W, but also with their fluo-compounds, among which ammo
fluo-molybdate $MoO_2F_2 2NH_4$ and others have long been known. (A few new sa
similar composition have been obtained by F. Moureu in 1893.) The action of per
of hydrogen upon these compounds gives salts containing a larger amount of oxygen
instance, a solution of $MoO_2F_2 2KFH_2O$ with peroxide of hydrogen gives a yellow
tion which after cooling separates out yellow crystalline flakes of $MoO_3F_2 2KFH_2O$, re
bling the salt originally taken in their external appearance. By employing a similar me
Piccini also obtained: $MoO_3F_2 2RbFH_2O$—yellow monoclinic crystals; $MoO_3F_2 2CsF$
—yellow flakes, and the corresponding tungstic compounds. All these salts re se
peroxide of hydrogen.

In speaking of these compounds I for my part think it may be well to call atte
to the fact that, in the first place, the composition of Piccini's oxy-fluo compounds
not correspond to that of permolybdic and pertungstic acid. If the latter be expr
by formulæ with one equivalent of an element, they will be $HMoO_4$ and HWO_4, an
oxy-fluo form corresponding to them should have the composition MoO_3F and
while it contains MO_3F_2 and WO_3F_2, *i.e.* answers as it were to a higher degree of
tion, MoH_2O_5 and $W HO_3$. But if permolybdic acid be regarded as $2MoO_3 + H_2$
as containing the elements of peroxide of hydrogen, then Piccini's compound will al
found to contain the original salts + H_2O; for example, from $MoO_2F_2 2KFH_2O$ th
obtained a compound $MoO_2F_2 2KFH_2O_2$, *i.e.* instead of H_2O they contain H_2O_2. I
second place the capacity of the salts of molybdenum and tungsten to retain a fu
amount of oxygen or H_2O_2 probably bears some relation to their property of giving
plex acids and of polymerising which has been considered in Note 8 bis. The
however, a great chemical interest in the accumulation of data respecting these
peroxide compounds corresponding to molybdic and tungstic acids. With regard t
peroxide form of uranium, *see* Chapter XX., Note 66.

[10] Uranium trioxide, or uranic oxide, shows its feeble basic and acid propertie
great number of its reactions. (1) Solutions of uranic salts give yellow precipitate
alkalis, but these precipitates do not contain the hydrate of the oxide, but compou
it with bases; for example, $2UO_2(NO_3)_2 + 6KHO = 4KNO_3 + 3H_2O + K_2U_2O_7$. Ther
other *urano-alkali compounds* of the same constitution; for example, (NH_4)
(known commercially as uranic oxide), MgU_2O_7, BaU_2O_7. They are the analogues
dichromates. Sodium uranate is the most generally used under the name of ur
yellow, $Na_2U_2O_7$. It is used for imparting the characteristic yellow green tint t
and porcelain. Neither heat nor water nor acids are able to extract the alkal
sodium uranate, $Na_2U_2O_7$, and therefore it is a true insoluble salt, of a yellow colou
clearly indicates the acid character (although feeble) of uranic oxide. (2) The carb
of the alkaline earths (for instance, barium carbonate) precipitate uranic oxide fro
salts, as they do all the salts of feeble bases; for example, R_2O_3. (3). The *alkalin*
bonates, when added to solutions of uranic salts, give a *precipitate, which is solu*

forming fluorescent yellowish-green salts of the composition
and in this respect uranic trioxide, UO_3, differs from chromic an
CrO_3, although the latter is able to give the oxychloride, CrO_2
molybdenum and tungsten, however, we see a clear transit
chromium to uranium. Thus, for example, chromyl chloride,
is a brown liquid which volatilises without change, and is co
decomposed by water; molybdenum oxychloride, MoO_2Cl_2, is
talline substance of a yellow colour, which is volatile and s
water (Blomstrand), like many salts. Tungsten oxychloride,
stands still nearer to uranyl chloride in its properties; it form
scales on which water and alkalis act, as they do on many s
chloride, ferric chloride, aluminium chloride, stannic chloride,
perfectly corresponds with the difficultly-volatile salt, UO_2Cl_2 (
by Peligot by the action of chlorine on ignited uranium dioxid
which is also yellow and gives a yellow solution with water, lik

an excess of the reagent, and particularly so if the acid carbonates be take
due to the fact that (4) the uranyl salts *easily form double salts* with the s
alkali metals, including the salts of ammonium. Uranium, in the form of th
salts, often gives salts of well-defined crystalline form, although the simple sal
prone to appear in crystals. Such, for example, are the salts obtained by dissol
sium uranate, $K_2U_2O_7$, in acids, with the addition of potassium salts of the s
Thus, with hydrochloric acid and potassium chloride a well-formed cryst
$K_2(UO_2)Cl_4,2H_2O$, belonging to the monoclinic system, is produced. This s
poses in dissolving in pure water. Among these double salts we may m
double carbonate with the alkalis, $R_4(UO_2)(CO_3)_3$ (equal to $2R_2CO_3 + UO_2$
acetates, $R(UO_2)(C_2H_3O_2)_3$—for instance, the sodium salt, $Na(UO_2)(C_2H_3O_2$
potassium salt, $K(UO_2)(C_2H_3O_2)_3,H_2O$; the sulphates, $R_2(UO_2)(SO_4)_2,2H_2O$, &
preceding formula $R = K, Na, NH_4$, or $R_2 = Mg, Ba$, &c. *This property*
comparatively stable double salts indicates feebly developed basic properti
double salts are mainly formed by salts of distinctly basic metals (these form,
the basic element of a double salt) and salts of feebly energetic bases (these for
element of a double salt), just as the former also give acid salts; the acid o
salts is replaced in the double salts by the salt of the feebly energetic base,
water, belongs to the class of intermediate bases. For this reason barium
give double salts with alkalis as magnesium does, and this is why double
more easily formed by potassium than by lithium in the series of the alk
(5) The most remarkable property, proving the feeble energy of uranic oxide a
seen in the fact that when their composition is compared with that of other sal
uranic oxide *always appear as basic salts*. It is well known that a normal
corresponds with the oxide R_2O_3, where $X = Cl, NO_3$, &c., or $X_2 = SO_4, CO_3$, &c.
also exist basic salts of the same type where $X = HO$ or $X_2 = O$. We saw s
kinds among the salts of aluminium, chromium, and others. With uranic oxi
are known of the types UX_6 (UCl_6, $U(SO_4)_3$, alums, &c., are not known), nor
U(HO)X, or UOX, but it always forms salts of the type U(HO)X

salts UO_2X_2. The property of uranic oxide, UO_3, of forming UO_2X_2 is shown in the fact that the hydrated oxide of uran $UO_2(HO)_2$, which is obtained from the nitrate, carbonate, and o salts by the loss of the elements of the acid, is easily soluble in a as well as in the fact that the lower grades of oxidation of uranium able, when treated with nitric acid, to form an easily crystallis uranyl nitrate, $UO_2(NO_3)_2,6H_2O$; this is the most commonly occur uranium salt.[11]

Uranium, which gives an oxide, UO_3, and the corresponding UO_2X_2 and dioxide UO_2, to which the salts UX_4 correspond, is ra met with in nature. Uranite or the double orthophosphate of ur

[11] *Uranyl nitrate*, or uranium nitrate, $UO_2(NO_3)_2,6H_2O$, crystallises from its tions in transparent yellowish-green prisms (from an acid solution), or in tabular cry (from a neutral solution), which effloresce in the air and are easily soluble in w alcohol, and ether, have a sp. gr. of 2·8, and fuse when heated, losing nitric acid and w in the process. If the salt itself (Berzelius) or its alcoholic solution (Malagut heated up to the temperature at which oxides of nitrogen are evolved, there then rem a mass which, after being evaporated with water, leaves uranyl hydroxide, $UO_2(H$ (sp. gr. 5·93), whilst if the salt be ignited there remains the dioxide, UO_2, as a bric powder, which on further heating loses oxygen and forms the dark olive uranoso-ur oxide, U_3O_8. The solution of the nitrate obtained from the ore is purified in the foll manner: sulphurous anhydride is first passed through it in order to reduce the ars acid present into arsenious acid; the solution is then heated to 60°, and sulphure hydrogen passed through it; this precipitates the lead, arsenic, and tin, and cer other metals, as sulphides, insoluble in water and dilute nitric acid. This liquid is filtered and evaporated with nitric acid to crystallisation, and the crystals are dissol in ether. Or else the solution is first treated with chlorine in order to convert the for chloride (produced by the action of the hydrogen sulphide) into ferric chloride, oxides are then precipitated by ammonia, and the resultant precipitate, containing oxides Fe_2O_3,UO_3, and compounds of the latter with potash, lime, ammonia, and o bases present in the solution (the latter being due to the property of uranic oxide combining with bases), is washed and dissolved in a strong, slightly-heated solution ammonium carbonate, which dissolves the uranic oxide but not the ferric oxide solution is filtered, and on cooling deposits a well-crystallising *uranyl ammonium bonate*, $UO_2(NH_4)_4(CO_3)_3$, in brilliant monoclinic crystals which on exposure to air sl give off water, carbonic anhydride, and ammonia; the same decomposition is rea effected at 300°, the residue then consisting of uranic oxide. This salt is not very solu in water, but is readily so in ammonium carbonate; it is obvious that it may readily converted into all the other salts of oxides of uranium. Uranium salts are also puri in the form of *acetate*, which is very sparingly soluble, and is therefore directly prec tated from a strong solution of the nitrate by mixing it with acetic acid.

We may also mention the *uranyl phosphate*, $HUPO_6$, which must be regarded as orthophosphate in which two hydrogens are replaced by the radicle uranyl, UO_2, i e $H(UO_2)PO_4$. This salt is formed as a hydrated gelatinous yellow precipitate, on mix a solution of uranyl nitrate with disodium phosphate. The precipitation occurs in oxide, $R(UO_2)H_2P_2O_8,7H_2O$, where $R=Cu$ or Ca, uraniu $U(SO_4)_2,H_2O$, samarakite, and æschynite, are very rarely fou then only in small quantities. Of more frequent and a occurrence is the non-crystalline, earthy brown uranium ore k *pitchblende* (sp. gr. 7·2), which is mainly composed of the inter oxide, $U_3O_8=UO_2,2UO_3$. This ore is found at Joachimsthal in and in Cornwall. It usually contains a number of different ties, chiefly sulphides and arsenides of lead and iron, as well and silica compounds. In order to expel the arsenic and sulp roasted, ground, washed with dilute hydrochloric acid, which dissolve the uranoso-uranic oxide, U_3O_8, and the residue is d in nitric acid, which transforms the uranium oxide into the $UO_2(NO_3)_2$.

It must be observed that the oxide of uranium, first distin by Klaproth (1789), was for a long time regarded as able metallic uranium under the action of charcoal and other reducing (with the aid of heat). But the substance thus obtained was *uranium dioxide*, UO_2. The compound nature of this dioxide,[1] presence of oxygen in it, was demonstrated by Peligot (1841), by it with charcoal in a stream of chlorine. He thus obtained a *uranium tetrachloride*, UCl_4,[13] which, when heated with sodiu

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[12] Uranium dioxide, or *uranyl*, UO , which is contained in the salts UC the appearance and many of the properties of a metal. Uranic oxide may be re uranyl oxide, $(UO_2)O$, its salts as salts of this uranyl; its hydroxide, $(UO_2)H_2O_2$, tuted like CaH_2O_2. The green oxide of uranium, uranoso-uranic oxide (easily for uranic salts by the loss of oxygen), $U_3O_8=UO_2,2UO_3$, when ignited with ch hydrogen (dry) gives a brilliant crystalline substance of sp. gr. about 11·0 (Urlau appearance resembles that of metals, and decomposes steam at a red heat evolution of hydrogen; it does not, however, decompose hydrochloric or acid, but is oxidised by nitric acid. The same substance (*i.e.* uranium dioxide also obtained by igniting the compound $(UO_2)K_2Cl_4$ in a stream of hydrogen, to the equation $UO_2K_2Cl_4+H_2=UO_2+2HCl+2KCl$. It was at first regard metal. In 1841 Peligot found that it contained oxygen, because carbonic anhydride were evolved when it was ignited with charcoal in a stream of chlo from 272 parts of the substance which was considered to be metal he obtained of a volatile product containing 142 parts of chlorine. From this it was concl the substance taken contained an equivalent amount of oxygen. As 142 parts o correspond with 32 parts of oxygen, it followed that $272-32=240$ parts of m combined in the substance with 32 parts of oxygen, and also in the chlorine obtained with 142 parts of chlorine. These calculations have been made for accepted atomic weight of uranium ($U=240$, *see* Note 14). Peligot took anoth

metallic uranium as a grey metal, having a specific gravity liberating hydrogen from acids, with the formation of green ura salts, UX_4, which act as powerful reducing agents.[14]

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rated. The solution of uranous chloride in water is green. It is also formed b action of zinc and copper (forming cuprous chloride) on a solution of uranyl ch UO_2Cl_2, especially in the presence of hydrochloric acid and sal-ammoniac. Solutio uranyl salts are converted into uranous salts by the action of various reducing a and among others by organic substances or by the action of light, whilst the salt are converted into uranyl salts, UO_2X_2, by exposure to air or by oxidising agents tions of the green uranyl salts act as powerful reducing agents, and give a b wn pitate of the uranous hydroxide, UH_4O_4, with potash and other alkalis. The hyd is easily soluble in acids but not in alkalis. On ignition it does not form the because it decomposes water, but when the higher oxides of uranium are ignit stream of hydrogen or with charcoal they yield uranous oxide. Both it and the ch UCl_4 dissolve in strong sulphuric acid, forming a green salt, $U(SO_4)_2,2H_2O$. The salt, together with uranyl sulphate, $UO_2(SO_4)$, is formed when the green oxide, U dissolved in hot sulphuric acid. The salts obtained in the latter instance ar separated by adding alcohol to the solution, which is left exposed to the light, the al reduces the uranyl salt to uranous salt, an excess of acid being required. An exc water decomposes this salt, forming a basic salt, which is also easily produced other circumstances, and contains $UO(SO_4),2H_2O$ (which corresponds to the uranic

[14] The atomic weight of uranium was formerly taken as half the present one, U and the oxides U_2O_3, suboxide UO, and green oxide U_3O_4, were of the same types a oxides of iron. With a certain resemblance to the elements of the iron group, ura presents many points of distinction which do not permit its being grouped with Thus uranium forms a very stable oxide, $U_2O_3 (U = 120)$, but does not give the c sponding chloride U_2Cl_6 (Roscoe, however, in 1874 obtained UCl_5, like $MoCl_5$ and W and under those circumstances (the ignition of oxide of uranium mixed with charc a stream of chlorine), when the formation of this compound might be expected, it (U = 120) the chloride UCl_2, which is characterised by its volatility; this is not a perty, to such an extent, of any of the bichlorides, RCl_2, of the iron group.

The alteration or doubling of the atomic weight of uranium—i.e. the recognit U = 240—was made for the first time in the first (Russian) edition of this work (1871 in my memoir of the same year in Liebig's *Annalen*, on the ground that with an a weight 120, uranium could not be placed in the periodic system. I think it will not be s fluous to add the following remarks on this subject: (1) In the other groups (K—Rb Ca—Sr—Ba, Cl—Br—I) the acid character of the oxides decreases and their basic c ter increases with the rise of atomic weight, and therefore we should expect the same in the group Cr—Mo—W—U, and if CrO_3, MoO_3, WO_3 be the acids then we indeed find a decrease in their acid character, and therefore uranium tri UO_3, should be a very feeble anhydride, but its basic properties should also be feeble. Uranic oxide does indeed show these properties, as was pointed out above (10). (2) Chromium and its analogues, besides the oxides RO_3, also form lower gra oxidation RO_2, R_2O_3, and the same is seen in uranium; it forms UO_3, UO_2, U_2O their compounds. (3) Molybdenum and tungsten, in being reduced from RO_3, easil frequently give an intermediate oxide of a blue colour, and uranium shows the property; giving the so-called green oxide which, according to present views, be regarded as $U_3O_8 = UO_2 2UO_3$, analogous to Mo_3O_8. (4) The higher chlorides, possible for the elements of this group, are either unstable (WCl_6) or do not exist (Cr); but there is one single lower volatile compound, which is decomposed by w and liable to further reduction into a non-volatile chlorine product and the metal. same is observed in uranium, which forms an easily volatile chloride, UCl_4, decomp by water. (5) The high sp. gr. of uranium (18·6) is explained by its analogy to tung (sp. gr. 10·1). (6) For uranium, as for chromium and tungsten, yellow tints

As the salts of uranic oxide are reduced in the absence o
matter by the action of light, and as they impart a char
coloration to glass,[15] they find a certain application in photogr
glass work.

If we compare together the highly acid elements, sulphur,
and tellurium, of the uneven series, with chromium, moly
tungsten, and uranium of the even series, we find that the res
of the properties of the higher form RO_3 does not extend to
forms, and even entirely disappears in the elements, for
not the smallest resemblance between sulphur and chromium
analogues in a free state. In other words, this means that
periods, like Na, Mg, Al, Si, P, S, Cl, containing seven ele
not contain any near analogues of chromium, molybdenum,
therefore their true position among the other elements must b
for only in those large periods which contain two small per
whose type is seen in the period containing: K, Ca, Sc, Ti, V
Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br. These large period
Ca and Zn, giving RO, Sc, and Ga of the third group, T
giving RO_2, V and As forming R_2O_5, Cr and Se of the six
Mn and Br of the seventh group, and the remaining elem
Co, Ni, form connective members of the intermediate eighth
the description of the representatives of which we shall tu
following chapters. We will now proceed to describe *m*
Mn=55, as an element of the seventh group of the even serie
following after Cr=52, which corresponds with Br=80 to
degree that Cr does with Se=79. For chromium, selen
bromine very close analogues are known, but for mangane
none have been obtained—that is, it is the only representati
even series in the seventh group. In placing manganese

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dominate in the form RO_3, whilst the lower forms are green and blue. (7) Z
(1881) determined the vapour densities of uranous bromide, UBr_4, and ch
(19·4 and 13·2), and they were found to correspond to the formulæ given abo
they confirmed the higher atomic weight $U = 240$. Roscoe, a great autho
metals of this group, was the first to accept the proposed atomic weight
$U = 240$, which since Zimmermann's work has been generally recognised.

[15] Uranium glass, obtained by the addition of the yellow salt $K_2U_2O_7$ to
green yellow fluorescence, and is sometimes employed for ornaments; it
violet rays, like the other salts of uranic oxide—that is, it possesses an abso
trum in which the violet rays are absent. The index of refraction of the al
is altered, and they are given out again as greenish-yellow rays; hence, co
uranic acid, when placed in the violet portion of the spectrum, emit a gree
light, and this forms one of the best examples (another is found in a solution
sulphate) of the phenomenon of fluorescence. The rays of light which p
uranic compounds do not contain the rays which excite the phenomena of
and of chemical transformation, as the researches of Stokes prove.

halogens in one group, the periodic system of the elements only requires that it should bear an analogy to the halogens in the higher type of oxidation—*i.e.* in the salts and acids—whilst it requires that as great a difference should be expected in the lower types and elements as there exists between chromium or molybdenum and sulphur or selenium. And this is actually the case. The elements of the seventh group form a higher salt-forming oxide, R_2O_7, and its corresponding hydrate, HRO_4, and salts—for example, $KClO_4$. Manganese in the form of potassium permanganate, $KMnO_4$, actually presents a great analogy in many respects to potassium perchlorate, $KClO_4$. The analogy of the crystalline form of both salts was shown by Mitscherlich. The salts of permanganic acid are also nearly all soluble in water, like those of perchloric acid, and if the silver salt of the latter, $AgClO_4$, be sparingly soluble in water, so also is silver permanganate, $AgMnO_4$. The specific volume of potassium perchlorate is equal to 55, because its specific gravity=2·54; the specific volume of potassium permanganate is equal to 58, because its specific gravity=2·71. So that the volumes of equivalent quantities are in this instance approximately the same whilst the atomic volumes of chlorine (35·5/1·3=27) and manganese (55/7·5) are in the ratio 4 : 1. In a free state the higher acids $HClO_4$ and $HMnO_4$ are both soluble in water and volatile, both are powerful oxidisers—in a word, their analogy is still closer than that of chromic and sulphuric acids, and those points of distinction which they present also appear among the nearest analogues—for example, in sulphuric and telluric acids, in hydrochloric and hydriodic acids, &c. Besides Mn_2O_7 manganese gives a lower grade of oxidation, MnO_3, analogous to sulphuric and chromic trioxides, and with it corresponds potassium manganate, K_2MnO_4, isomorphous with potassium sulphate.[16] In the still lower grades of oxidation, Mn_2O_3 and MnO, there is hardly any similarity to chlorine, whilst every point of resemblance disappears when we come to the elements themselves—*i.e.* to manganese and chlorine—for manganese is a metal, like iron, which combines directly with chlorine to form a saline compound, $MnCl_2$, analogous to magnesium chloride.[17]

Manganese belongs to the number of metals widely distributed in

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[16] The comparison of potassium permanganate with potassium perchlorate or of

frequently contain compounds of manganous oxide, MnO, v
a resemblance to ferrous oxide, FeO, and to magnesia. In r
magnesia and the oxides allied to it are replaced by mang
calcspars and magnesites—*i.e.* $R''CO_3$ in general—are fr
with containing manganous carbonate, which also occurs
state, although but rarely. The soil also and the ash of pla
contain a small quantity of manganese. In the analysis
it is generally found that manganese occurs together w
because, like it, manganous oxide remains in solution in th
ammoniacal salts, not being precipitated by reagents. Th
this manganous oxide, MnO, of passing into the higher gra
tion under the influence of heat, alkalis, and air, gives an
not only of discovering the presence of manganese in adı
magnesia, but also of separating these two analogous bases.
not able to give higher grades of oxidation, whilst mangane
with great facility. Thus, for instance, an *alkaline* solut
hypochlorite produces a precipitate of manganese dioxide in
a manganous salt: $MnCl_2 + NaClO + 2NaHO = MnO_2 +$ I
whilst magnesia is not changed under these circumstances
in the form of $MgCl_2$. If the magnesia be precipitated
presence of alkali, it may be dissolved in acetic acid, in whic
dioxide is insoluble. The presence of small quantities
may also be recognised by the green coloration which al
when heated with manganese compounds in the air. This
tion depends on the property of manganese of giving a g
manganate: $MnCl_2 + 4KHO + O_2 = K_2MnO_4 + 2KCl + 2$
the faculty of oxidising in the presence of alkalis forms
character of manganese. The higher grades of oxidatio
Mn_2O_7 and MnO_3 are quite unknown in nature, and even
so widely spread in nature as the ores composed of mar
pounds which are met with nearly everywhere. The mo
ore of manganese is its dioxide, or so called *peroxide*, Mr
known in mineralogy as *pyrolusite*. Manganese also
oxide corresponding with magnetic iron ore, MnO,Mn
forming the mineral known as *hausmannite*. The oxide
occurs in nature as the anhydrous mineral *braunite*, and i
form, Mn_2O_3,H_2O, called *manganite*. Both of these ofte
admixture in pyrolusite. Besides which, manganese is
nature as a rose-coloured mineral, *rhodonite*, or silicate, Mr
fine and rich deposits of manganese ores have been f
Caucasus, the Urals, and along the Dnieper. Those at the

district of the Government of Kutais and at Nicopol on the Dnie are particularly rich. A large quantity of the ore (as much as 100, tons yearly) is exported from these localities.

Thus manganese gives oxides of the following forms M manganous oxide, and manganous salts, MnX_2, corresponding with base, which resembles magnesia and ferrous oxide in many respe Mn_2O_3, a very feeble base, giving salts, MnX_3, analogous to aluminium and ferric salts, easily reduced to MnX_2; MnO_2, diox generally called peroxide, an almost indifferent oxide, or feebly acid MnO_3, manganic anhydride, which forms salts resembling potass sulphate;[18 bis] Mn_2O_7, permanganic anhydride, giving salts analog to the perchlorates.

All the oxides of manganese when heated with acids give salts, Mn corresponding with the lower grade of oxidation, *manganous ox* MnO. Manganic oxide, Mn_2O_3, is a feebly energetic base; it is t that it dissolves in hydrochloric acid and gives a dark solution c taining the salt $MnCl_3$, but the latter when heated evolves chlor and gives a salt corresponding with manganous oxide $MnCl_2$—i.e. first; $Mn_2O_3+6HCl=3H_2O+Mn_2Cl_6$, and then the Mn_2Cl_6 deco poses into $2MnCl_2+Cl_2$. None of the remaining higher grades oxidation have a basic character, but *act as oxidising agents in presence of acids*, disengaging oxygen and passing into salts of the lo grade of oxidation of manganese, MnO. Owing to this circumstan *the manganous salts* are often obtained; they are, for instance, left the residue when the dioxide is used for the preparation of oxygen chlorine.[19]

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[18] The name 'peroxide' should only be retained for those *highest* oxides (and M stands between MnO and MnO_3) which either by a direct method of double decomposi are able to give hydrogen peroxide or contain a larger proportion of oxygen than base or the acid, just as hydrogen peroxide contains more oxygen than water. T type will be H_2O_2, and they are exemplified by barium peroxide, BaO_2, and sulp peroxide, S_2O_7, &c. Such a dioxide as MnO_2 is, in all probability, a salt—that manganous manganate, MnO_3MnO, and also, as a basic salt of a feeble base, capabl combining with alkalis and acids. Hence the name of manganese peroxide sho be abandoned, and replaced by manganese dioxide. PbO_2 is better termed lead dio than peroxide. Bisulphide of manganese, MnS_2, corresponding to iron pyrites, F sometimes occurs in nature in fine octahedra (and cube combinations), for instance Sicily; it is called Hauerite.

[18 bis] On comparing the manganates with the permanganates—for example, K_2M with $KMnO_4$—we find that they differ in composition by the

As the salts of manganous oxide MnX_2 closely resemble isomorphous with) the salts of magnesia MgX_2 in many respe

(from the native MnO_2), from which it cannot be freed by crystallisat removal may, however, be effected by mixing a portion of the liquid with a sodium carbonate; a precipitate of manganous carbonate is then formed. cipitate is collected and washed, and then added to the remaining mass of solution of manganous sulphate; on heating the solution with this prec whole of the iron is precipitated as oxide. This is due to the fact that in the the manganese dioxide in sulphuric acid the whole of the iron is converte ferric state (because the dioxide acts as an oxidising agent), which, as an feeble base precipitated by calcium carbonate and other kindred salts, is also p by manganous carbonate. After being treated in this manner, the solution of sulphate is further purified by crystallisation. If it be a bright red colour, the presence of higher grades of oxidation of manganese; they may be de boiling the solution, when the oxygen from the oxides of manganese is evol very faintly coloured solution of manganous sulphate is obtained. This salt is for the facility with which it gives various combinations with water. By e the almost colourless solution of *manganous sulphate* at very low temperatur cooling the saturated solution at about 0°, crystals are obtained containing water of crystallisation, $MnSO_4,7H_2O$, which are isomorphous with cobaltous sulphates. These crystals, even at 10°, lose 5 p.c. of water, and completely 15°, losing about 20 p.c. of water. By evaporating a solution of the salt at t temperature, but not above 20°, crystals are obtained containing 5 mol. are isomorphous with copper sulphate; whilst if the crystallisation be carried 20° and 30°, large transparent prismatic crystals are formed containing 4 mo Nickel). A boiling solution also deposits these crystals together with crystals 3 mol. H_2O, whilst the first salt, when fused and boiled with alcohol, giv containing 2 mol. H_2O. Graham obtained a monohydrated salt by drying about 200°. The last atom of water is eliminated with difficulty, as in the c salts like $MgSO_4,nH_2O$. The crystals containing a considerable amount o rose coloured, and the anhydrous crystals are colourless. The solubility of M (Chapter I., Note 24) per 100 parts of water is: at 10°, 127 parts; at 37·5°, 1 75°, 145 parts; and at 101°, 92 parts. Whence it is seen that at the boiling p is less soluble than at lower temperatures, and therefore a solution satur ordinary temperature becomes turbid when boiled. Manganous sulphate, bein to magnesium sulphate, is decomposed, like the latter, when ignited, but it d leave manganous oxide, but the intermediate oxide, Mn_3O_4. It gives doubl the alkali sulphates. With aluminium sulphate it forms fine radiated cry composition resembles that of the alums—namely, $MnAl_2(SO_4)_4,24H_2O$. easily soluble in water, and occurs in nature.

Manganous chloride, MCl_2, crystallises with 4 mol H_2O, like the ferro not with 6 mol H_2O like many kindred salts—for example, those of cobalt, magnesium; 100 parts of water dissolve 38 parts of the anhydrous salt at parts at 62°. Alcohol also dissolves manganous chloride, and the alcoh burns with a red flame. This salt, like magnesium chloride, readily forms A solution of borax gives a dirty rose coloured precipitate having the $MnH_4(BO_3)_2H_2O$, which is used as a drier in paint making. Potassium c duces a yellowish grey precipitate, MnC_2N_2, with manganous salts, soluble in the reagent, a double salt, $K_4MnC_6N_6$, corresponding with potassium f being formed. On evaporation of this solution, a portion of the manganese and precipitated, whilst a salt corresponding to Gmelin's red salt, K Chapter XXII.), remains in solution. Sulphuretted hydrogen does n salts of manganese, not even the acetate, but ammonium sulphide gives a

the exception of the fact that MnX_2 are rose coloured and are
oxidised in the presence of alkalis), we will not dwell upon them

oxalate, MnC_2O_4. This precipitate is insoluble in water, and is used for the prep
of manganous oxide itself because it decomposes like oxalic acid when ignited (in
without access of air), with the formation of carbonic anhydride, carbonic oxid
manganous oxide. *Manganous oxide* thus obtained is a green powder, which h
oxidises with such facility that it burns in air when brought into contact w
incandescent substance, and passes into the red intermediate oxide Mn_3O_4. In sol
of manganous salts, alkalis produce a precipitate of the hydroxide MnH_2O_2,
rapidly absorbs oxygen in the presence of air and gives the brown intermediate
or, more correctly speaking, its hydrate.

Manganous oxide, besides being obtained by the above-described method from
ganous oxalate, may also be obtained by igniting the higher oxides in a stre
hydrogen, and also from manganese carbonate. The manganous oxide ignited
presence of hydrogen acquires a great density, and is no longer so easily oxidise
may also be obtained in a crystalline form, if during the ignition of the carbon
higher oxide a trace of dry hydrochloric acid gas be passed into the current of hyd
It is thus obtained in the form of transparent emerald green crystals of the r
system, and in this state is easily soluble in acids.

Manganous oxide in oxidising gives the *red oxide of manganese*, Mn_3O_4. This
most stable of all the oxides of manganese; it is not only stable at the ordinary bu
at a high temperature—that is, it does not absorb or disengage oxygen spontane
When ignited, all the higher oxides of manganese pass into it by losing oxygen
manganous oxide by absorbing oxygen. This oxide does not give any distinct
but it dissolves in sulphuric acid, forming a dark red solution, which contains
manganous and manganic (of the *oxide*, Mn_2O_3) sulphates. The latter with pota
sulphate gives a manganese alum, in which the alumina is replaced by its isomor
oxide of manganese. But this alum, like the solution of the intermediate oxide in
phuric acid, evolves oxygen and leaves a manganous salt when slightly heated

Manganese dioxide is still less basic than the oxide, and disengages oxygen
halogen in the presence of acids, forming manganous salts, like the oxide However
be suspended in ether, and hydrochloric acid gas passed into the mixture, which is
cool, the ether acquires a green colour, owing to the formation of tetra chlor
manganese, $MnCl_4$, corresponding with the dioxide which passes into solution.
however very unstable, being exceedingly easily decomposed with the evolutio
chlorine. The corresponding fluoride, MnF_4, obtained by Nicklès is much more st
At all events, manganese dioxide does not exhibit any well defined basic characte
has rather an acid character, which is particularly shown in the compounds MnF
$MnCl_4$ just mentioned, and in the property of manganese dioxide of combining
alkalis. If the higher grades of oxidation of manganese be deoxidised in the presen
alkalis, they frequently give the dioxide combined with the alkali for example, in
presence of potash a compound is formed which contains $K_2O,5MnO_2$, which show
weak acid character of this oxide. When ignited in the presence of sodium compo
manganese dioxide frequently forms $Na_2O,8MnO_2$ and $Na_2O,12MnO_2$, and lime w
heated with MnO_2 gives from $CaO,3MnO_2$ to $(CaO)_3,MnO_2$ (Rousseau) according t
temperature. Besides which, perhaps, MnO_2 is a saline compound, contai
$MnOMnO_3$ or $(MnO)_3Mn_2O_7$, and there are reactions which support such a view (Sp
Richards, Traube, and others); for instance it is known that manganous chloride

limit ourselves to illustrating the chemical character of mang describing the metal and its corresponding acids. The fact a the oxides of manganese are not reduced to the metal when i hydrogen (whilst the oxides of iron give metallic iron unc circumstances), but only to manganous oxide, MnO, sho manganese has a considerable affinity for oxygen—that is, it i to reduce. This may be effected, however, by means of cha sodium at a very high temperature. A mixture of one of the manganese with charcoal or organic matter gives fused *meta ganese* under the powerful heat developed by coke with an draught. The metal was obtained for the first time in this m Gahn, after Pott, and more especially Scheele, had in the last shown the difference between the compounds of iron and m (they were previously regarded as being the same). Manganes pared by mixing one of its oxides in a finely-divided state with soot; the resultant mass is then first ignited in order to de the organic matter, and afterwards strongly heated in a charcoal The manganese thus obtained, however, contains, as a rule, a able amount of silicon and other impurities. Its specific gravi between 7·2 and 8·0. It has a light grey colour, a feebly lustre, and although it is very hard it can be scratched by a rapidly oxidises in air, being converted into a black oxide; w on it with the evolution of hydrogen—this decomposition proc rapidly with boiling water, and if the metal contain carbon.[20]

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dioxide, as was mentioned above. Manganous nitrate also leaves mangan when heated to 200°. It is also obtained from manganous and manganic s alkalis, when they are decomposed in the presence of a small amount of acid tical method of converting the salts MnX_2 into the higher grades of oxidation Chapter II., Note 6.

[20] Other chemists have obtained manganese by different methods, and different properties to it. This difference probably depends on the presence in different proportions. Deville obtained manganese by subjecting the pu mixed with pure charcoal (from burnt sugar), to a strong heat in a lime cru resultant metal fused. The metal obtained had a rose tint, like bismuth, was very brittle, although exceedingly hard. It decomposed water at th temperature. Brunner obtained manganese having a specific gravity of about

It has been shown above that if manganese dio
lower oxide of manganese, be heated with an alkali in t
air, the mixture absorbs oxygen,[21] and forms an alkaline m
green colour: $2KHO + MnO_2 + O = K_2MnO_4 + H_2O$. St
gaged during the ignition of the mixture, and if this
place there is no absorption of oxygen. The oxidation p
more rapidly if, before igniting in air, potassium chlor
added to the mixture, and this is the method of prepar
manganate, K_2MnO_4. The resultant mass dissolved in a
of water gives a dark green solution, which, when evapor
receiver of an air pump over sulphuric acid, deposits gre
exactly the same form as potassium sulphate—namely, si
and pyramids. The composition of the product is not ch
redissolved, if perfectly pure water free from air and ca
taken. But in the presence of even very feeble acids
this salt changes its colour and becomes red, and depos
dioxide. The same decomposition takes place when the
with water, but when diluted with a large quantity of
manganese dioxide does not separate, although the solu
This change of colour depends on the fact that potassiu
K_2MnO_4, whose solution is green, is transformed into
manganate, $KMnO_4$, whose solution is of a red colour.
proceeding under the influence of acids and a large qua

furnace, obtained carbides of manganese—for example, Mn_3C—and rema
volatilised in the heat of the voltaic arc. Metallic manganese is, howev
a large scale, but only its alloys with carbon (they readily and rapidly
manganese or a coarsely crystalline alloy of iron, manganese and
smelted in blast-furnaces like pig iron (see Chapter XXII.) This
employed in the manufacture of steel by Bessemer's and other proc
XXII.) and for the manufacture of manganese bronze. However, in A
Wald (1895) obtained almost pure metallic manganese on a large scal
the ore of MnO_2 with 30 p.c. sulphuric acid (which extracts all
present in the ore), and then heat it in a reducing flame to convert
they mix with a powder of Al, lime and CaF_2 (as a flux), and hea
crucible lined with magnesia; a reaction immediately takes place at a
and a metal of specific gravity 7·3 is obtained, which only contains

Manganese gives two compounds with *nitrogen*, Mn_5N_2 and M
obtained by Prelinger (1894) from the amalgam of manganese Mn_2
mercury anode by the action of an electric current upon a soluti
mercury may be removed from this amalgam by heating it in an atmo
and then metallic manganese is obtained as a grey porous mass of
If this amalgam be heated in dry nitrogen it gives Mn_5N_2 (grey pow
if heated in an atmosphere of NH_3 it gives (as also does Mn_5N_2) M
with a metallic lustre, sp. gr. 6·21), which, when heated in nitroge
Mn_5N_2, and if heated in hydrogen evolves NH_3 and disengages hydro
of NH_4Cl. At all events, manganese is a metal which decompose
than iron, nickel, and cobalt.

[21] Volume I. p. 157, Note 7.

is expressed in the following manner: $3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KHO$. If there is a large proportion of acid and the decomposition is aided by heat, the manganese dioxide and potassium permanganate are also decomposed, with formation of manganous salt. Exactly the same decomposition as takes place under the action of acids is also accomplished by magnesium sulphate, which reacts in many cases like an acid. When water holding atmospheric oxygen in solution acts on a solution of potassium manganate, the oxygen combines directly with the manganate and forms potassium permanganate, without precipitating manganese dioxide, $2K_2MnO_4 + O + H_2O = 2KMnO_4 + 2KHO$. Thus a solution of potassium manganate undergoes a very characteristic change in colour and passes from green to red; hence this salt received the name of *chameleon mineral*.[23]

Potassium permanganate, $KMnO_4$, crystallises in well-formed, long red prisms with a bright green metallic lustre. In the arts the potash is frequently replaced by soda, and by other alkaline bases, but no salt of permanganic acid crystallises so well as the potassium salt, and therefore this salt is exclusively used in chemical laboratories. One part of the crystalline salt dissolves in 15 parts of water at the ordinary temperature. The solution is of a very deep *red colour*, which is so intense that it is still clearly observable after being highly diluted with water. In a solid state it is decomposed by heat, with evolution of oxygen, a residue consisting of the lower oxides of manganese and potassium oxide being left.[22 bis] A mixture of permanganate of potassium, phosphorous and sulphur takes fire when struck or rubbed, a mixture of the permanganate with carbon only takes fire when heated, not when struck. The instability of the salt is also seen in the fact that its solution is decomposed by peroxide of hydrogen, which at the same time it decomposes. A number of substances reduce potassium permanganate to manganese dioxide (in which case the red solution becomes colourless).[23] Many organic substances (although far from all, even when boiled in a solution of permanganate) act in this manner, being oxidised at the expense of a portion of its oxygen. Thus, a solution of sugar decomposes a cold solution of potassium permanganate. In the presence of an excess of alkali, with a small quantity of sugar, the reduction leads to the formation of potassium manganate, because $2KMnO_4 + 2KHO = O + 2K_2MnO_4 + H_2O$. With a considerable amount of sugar and a more prolonged action, the solution turns brown and precipitates manganese dioxide or even oxide. In the oxidation of many organic bodies by an alkaline solution of $KMnO_4$ generally three-eighths of the oxygen in the salt are utilised for oxidation: $2KMnO_4 = K_2O + 2MnO_2 + O_3$. A portion of the alkali liberated is retained by the manganese dioxide, and the other portion generally combines with the substance oxidised, because the latter most frequently gives an acid with an excess of alkali. A solution of potassium iodide acts in a similar manner, being converted into potassium iodate at the expense of the three atoms of oxygen disengaged by two molecules of potassium permanganate.

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[23] It was known to the alchemists by this name, but the true explanation of the change in colour is due to the researches of Chevillot, Edwards, Mitscherlich, and Forchhammer. The change in colour of potassium manganate is due to its instability and to its splitting up into two other manganese compounds, a higher and a lower $3MnO_3 = Mn_2O_7 + MnO_2$. Manganese trioxide is really decomposed in this manner by the action of water (see later): $3MnO_3 + H_2O = 2MnHO_4 + MnO_2$ (Franke, Thorpe, and Humbly). The instability of the salt is proved by the fact of its being deoxidised by organic matter, with the formation of manganese dioxide and alkali, so that, for instance, a solution of this salt cannot be filtered through paper. The presence of an excess of alkali increases the stability of the salt; when heated it breaks up in the presence of water, with the evolution of oxygen.

The method of preparing *potassium permanganate* will be understood from the above. There are many recipes for preparing this substance, as it is now used in considerable quantities both for technical and laboratory purposes. But in all cases the essence of the methods is one and the same: a mixture of alkali with any oxide of manganese (even manganous hydroxide, which may be obtained from manganous chloride) is first heated in the presence of air or of an oxidising substance (for the sake of rapidity, with potassium chlorate), the resultant mass is then treated with water and heated, when manganese dioxide is precipitated and potassium permanganate remains in solution. This solution may be boiled, as the liquid will contain free alkali; but the solution cannot be evaporated to dryness, because a strong solution, as well as the solid salt, is decomposed by heat

By adding a dilute solution of manganous sulphate to a boiling mixture of lead dioxide and dilute nitric acid, the whole of the manganese may be converted into permanganic acid (Crum)

In the presence of acids, potassium permanganate acts as an oxidising agent with still greater energy than in the presence of alkalis. At any rate, a greater proportion of oxygen is then available for oxidation, namely, not $\frac{3}{8}$, as in the presence of alkalis, but $\frac{5}{8}$, because in the first instance manganese dioxide is formed, and in the second case manganous oxide, or rather the salt, MnX_2, corresponding with it. Thus, for

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[22 bis] The solution of this salt with an excess of impure commercial alkali generally acquires a green tint.

[23] A solution of potassium permanganate gives a beautiful absorption spectrum (Chapter XIII.) If the light in passing through this solution loses a portion of its rays in it (if one may so account for it), this is partially explained by the increased oxidising power which the solution then acquires. We may here also remark that a dilute solution of permanganate of potassium forms a colourless solution with nickel salts, because the green colour of the solution of nickel salts is complementary to the red. Such a decolorised solution, containing a large proportion of nickel and a small proportion of manganese, decomposes after a time, throws down a precipitate, and re-acquires the green colour proper to the nickel salts. The addition of a solution of a cobalt salt (rose-red) to the nickel salt also destroys the colour of both salts.

instance, in the presence of an excess of sulphuric acid, the decomposition is accomplished in the following manner: $2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$. This decomposition, however, does not proceed directly on mixing a solution of the salt with sulphuric acid, and crystals of the salt even dissolve in oil of vitriol without the evolution of oxygen, and this solution only decomposes by degrees after a certain time. This is due to the fact that sulphuric acid liberates free permanganic acid from the permanganate,[24] which acid is stable in solution. But if, in the presence of acids and a permanganate, there is a substance capable of absorbing oxygen—for instance, capable of passing into a higher grade of oxidation—then the reduction of the permanganic acid into manganous oxides sometimes proceeds directly at the ordinary temperature. This reduction is very clearly seen, because the solutions of potassium permanganate are red whilst the manganous salts are almost colourless. Thus, for instance, nitrous acid and its salts are converted into nitric acid and decolorise the acid solution of the permanganate. Sulphurous anhydride and its salts immediately decolorise potassium permanganate, forming sulphuric acid. Ferrous salts, and in general salts of lower grades of oxidation capable of being oxidised in solution, act in exactly the same manner. Sulphuretted hydrogen is also oxidised to sulphuric acid; even mercury is oxidised at the expense of permanganic acid, and decolorises its solution, being converted into mercuric oxide. Moreover, the end point of these reactions may easily be seen, and therefore, having first determined the amount of active oxygen in one volume of a solution of potassium permanganate, and knowing how many volumes are required to effect a given oxidation, it is easy to determine the amount of an oxidisable substance in a solution from the amount of permanganate expended (Marguerite's method).

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[24] If sulphuric acid is allowed to act on potassium permanganate without any special precautions, a large amount of oxygen is evolved (it may even explode and inflame), and a violet spray of the decomposing permanganic acid is given off. But if the pure salt (i.e. free from chlorine) be dissolved in pure well-cooled sulphuric acid, without any rise in temperature, a green-coloured liquid settles at the bottom of the vessel. This liquid does not contain any sulphuric acid, and consists of permanganic anhydride, Mn_2O_7 (Aschoff, Terreil). It is impossible to prepare any considerable quantity of the anhydride by this method, as it decomposes with an explosion as it collects, evolving oxygen and leaving red oxide of manganese. *Permanganic anhydride*, Mn_2O_7, in dissolving in sulphuric acid, gives a green solution, which (according to Franke, 1887) contains a compound $Mn_2SO_{10} = (MnO_3)_2SO_4$—that is, sulphuric acid in which both hydrogens are replaced by the group MnO_3, which is combined with OK in permanganate of potassium. This mixture with a small quantity of water gives Mn_2O_7, according to the equation: $(MnO_3)_2SO_4 + H_2O = H_2SO_4 + Mn_2O_7$, and when heated to 30° it gives *manganese trioxide*, $(MnO_3)_2SO_4 + H_2O = 2MnO_3 + H_2SO_4 + O$. Pure manganese trioxide is obtained if the solution of $(MnO_3)_2SO_4$ be poured in drops on to sodium carbonate. Then, together with carbonic anhydride, a spray of manganese trioxide passes over, which may be collected in a well cooled receiver, and this shows that the reaction proceeds according to the equation: $(MnO_3)_2SO_4 + Na_2CO_3 = Na_2SO_4 + 2MnO_3 + CO_2 + O$ (Thorpe). The trioxide is decomposed by water, forming manganese dioxide and a solution of *permanganic acid*: $3MnO_3 + H_2O = MnO_2 + 2HMnO_4$. The same acid is obtained by dissolving permanganic anhydride in water.

Barium permanganate when treated with sulphuric acid gives the same acid. This barium salt may be prepared by the action of barium chloride on the difficultly soluble silver permanganate, $AgMnO_4$, which is precipitated on mixing a strong solution of the potassium salt with silver nitrate. The solution of permanganic acid forms a bright red liquid which reflects a dark violet tint. A dilute solution has exactly the same colour as that of the potassium salt. It deposits manganese dioxide when exposed to the action of light, and also when heated above 60°, and this proceeds the more rapidly the more dilute the solution. It shows its oxidising properties in many cases, as already mentioned. Even hydrogen gas is absorbed by a solution of permanganic acid; and charcoal and sulphur are also oxidised by it, as they are by potassium permanganate. This may be taken advantage of in analysing gunpowder, because when it is treated with a solution of potassium permanganate, all the sulphur is converted into sulphuric acid and all the charcoal into carbonic anhydride. Finely divided platinum immediately decomposes permanganic acid. With potassium iodide it liberates iodine (which may afterwards be oxidised into iodic acid) (Mitscherlich, Fromherz, Aschoff, and others). Ammonia does not form a corresponding salt with free permanganic acid, because it is oxidised with evolution of nitrogen. The oxidising action of permanganic acid in a strong solution may be accompanied by flame and the formation of violet fumes of permanganic acid; thus a strong solution of it takes fire when brought into contact with paper, alcohol, alkaline sulphides, fats, &c.

We may add that, according to Franke, 1 part of potassium permanganate with 18

The oxidising action of $KMnO_4$, like all other chemical reactions, is not accomplished instantaneously, but only gradually. And, as the course of the reaction is here easily followed by determining the amount of salt unchanged in a sample taken at a given moment,[25] the oxidising reaction of potassium permanganate, in an acid liquid, was employed by Harcourt and Esson (1865) as one of the first cases for the investigation of the laws of the *rate of chemical change*[26] as a subject of great importance in chemical mechanics. In their experiments they took oxalic acid,

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parts of sulphuric acid at 100° gives brown crystals of the salt $Mn_2(SO_4)_3,H_2SO_4,4H_2O$, which gives a precipitate of hydrated manganese dioxide, $H_2MnO_3 = MnO_2,H_2O$, when treated with water.

Spring, by precipitating potassium permanganate with sodium sulphite and washing the precipitate by decantation, obtained a soluble colloidal manganese oxide, whose composition was the mean between Mn_2O_3 and MnO_2—namely, $Mn_2O_3,4(MnO_2),H_2O$.

[25] For rapid and accurate determinations of this kind, advantage is taken of those methods of chemical analysis which are known as 'titrations' (volumetric analysis), and consist in measuring the volume of solutions of known strength required for the complete conversion of a given substance. Details respecting the theory and practice of titration, in which potassium permanganate is very frequently employed, must be looked for in works on analytical chemistry.

[26] The measurements of velocity and acceleration serve for determining the measure of forces in mechanics, but in that case the velocities are magnitudes of length or paths passed over in a unit of time. The velocity of chemical change embodies a conception of quite another kind. In the first place, the velocities of reactions are magnitudes of the masses which have entered into chemical transformations; in the second place, these velocities can only be relative quantities. Hence the conception of 'velocity' has quite a

$C_2H_2O_4$, which in oxidising gives carbonic anhydride, whilst, with an excess of sulphuric acid, the potassium permanganate is converted into manganous sulphate, $MnSO_4$, so that the ultimate oxidation will be expressed by the equation: $5C_2H_2O_4 + 2MnKO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$. The influence of the relative amount of sulphuric acid is seen from the annexed table, which gives the measure of reaction p per 100 parts of potassium permanganate, taken four minutes after mixing, using n molecules of sulphuric acid, H_2SO_4, per $2KMnO_4 + 5C_2H_2O_4$

$n =$	2	4	6	8	12	16	22
$p =$	22	36	51	63	77	86	92

showing that in a given time (4 minutes) the oxidation is the more perfect the greater the amount of sulphuric acid taken for given amounts of $KMnO_4$ and $C_2H_2O_4$. It is obvious also that the temperature and relative amount of every one of the acting and resulting substances should show its influence on the relative velocity of reaction; thus, for instance, direct experiment showed the influence of the admixture of manganous sulphate. When a large proportion of oxalic acid (108 molecules) was taken to a large mass of water and to 2 molecules of permanganate 14 molecules of manganous sulphate were added, the quantity x of the potassium permanganate acted on (in percentages of the potassium permanganate taken) in t minutes (at 16°) was as follows:

$t =$	2	5	8	11	14	44	47	53	61	68
$x =$	5·2	12·1	18·7	25·1	31·3	68·4	71·7	75·8	79·8	83·0

These figures show that the rate of reaction—that is, the quantity of permanganate changed in one minute—decreases proportionally to the decrease in the amount of unchanged potassium permanganate. At the

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different meaning in chemistry from what it has in mechanics. Their only common factor is time. If dt be the increment of time and dx the quantity of a substance changed in this space of time, then the fraction (or quotient) dx/dt will express the rate of the reaction. The natural conclusion, come to both by Harcourt and Esson, and previously to them (1850) by Wilhelmy (who investigated the rate of conversion, or inversion, of sugar in its passage into glucose), consists in establishing that this velocity is proportional to the quantity of substances still unchanged—or that $dx/dt = C(A - x)$, where C is a constant coefficient of proportionality, and where A is the quantity of a substance taken for reaction at the moment when $t = 0$ and $x = 0$—that is, at the beginning of the experiment, from which the time t and quantity x of substance changed is counted. On integrating the preceding equation we obtain $\log(A/A - x) = kt$, where k is a new constant, if we take ordinary (and not natural) logarithms. Hence, knowing A, x, and t, for each reaction, we find k, and it proves to be a constant quantity. Thus from the figures cited in the text for the reaction $2KMnO_4 + 108C_2H_2O_4 + 14MnSO_4$, it may be calculated that $k = 0·0114$; for example, $t = 44$, $x = 68·4$ ($A = 100$), whence $kt = 0·5004$ and $k = 0·0114$, (*see also* Chapter XIV., Note 3, and Chapter XXVII., Note 25 *bis*).

commencement, about 2·6 per cent. of the salt taken was decomposed in the course of one minute, whilst after an hour the rate was about 0·5 per cent. The same phenomena are observed in every case which has been investigated, and this branch of theoretical or physical chemistry, now studied by many,[27] promises to explain the course of chemical transformations from a fresh point of view, which is closely allied to the doctrine of affinity, because the rate of reaction, without doubt, is connected with the magnitude of the affinities acting between the reacting substances.

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[27] The researches made by Hood, Van't Hoff, Ostwald, Warder, Menschutkin, Konovaloff, and others have a particular significance in this direction. Owing to the comparative novelty of this subject, and the absence of applicable as well as indubitable deductions, I consider it impossible to enter into this province of theoretical chemistry, although I am quite confident that its development should lead to very important results, especially in respect to chemical equilibria, for Van't Hoff has already shown that the limit of reaction in reversible reactions is determined by the attainment of equal velocities for the opposite reactions.

CHAPTER XXII

IRON, COBALT, AND NICKEL

JUDGING from the atomic weights, and the forms of the higher oxides of the elements already considered, it is easy to form an idea of the seven groups of the periodic system. Such are, for instance, the typical series Li, Be, B, C, N, O, F, or the third series, Na, Mg, Al, Si, P, S, Cl. The seven usual types of oxides from R_2O to R_2O_7 correspond with them (Chapter XV.) The position of the eighth group is quite separate, and is determined by the fact that, as we have already seen, in each group of metals having a greater atomic weight than potassium a distinction ought to be made between the elements of the even and uneven series. The series of even elements, commencing with a strikingly alkaline element (potassium, rubidium, cæsium), together with the uneven series following it, and concluding with a haloid (chlorine, bromine, iodine), forms a large period, the properties of whose members repeat themselves in other similar periods. The elements of the eighth group are situated between the elements of the even series and the elements of the uneven series following them. And for this reason elements of the eighth group are found in the middle of each large period. The properties of the elements belonging to it, in many respects independent and striking, are shown with typical clearness in the case of iron, the well-known representative of this group.

Iron is one of those elements which are not only widely diffused in the crust of the earth, but also throughout the entire universe. Its oxides and their various compounds are found in the most diverse portions of the earth's crust; but here iron is always found combined with some other element. Iron is not found on the earth's surface in a free state, because it easily oxidises under the action of air. It is occasionally found in the native state in meteorites, or aerolites, which fall upon the earth.

Meteoric iron is formed outside the earth.[1] Meteorites are fragments which are carried round the sun in orbits, and fall upon the earth when coming into proximity with it during their motion in space. The meteoric dust, on passing through the upper parts of the atmosphere, and becoming incandescent from friction with the gases, produces that phenomenon which is familiar under the name of falling stars.[3] Such is

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[1] The composition of meteoric iron is variable. It generally contains nickel, phosphorus, carbon, &c. The schreibersite of meteoric stones contains Fe_4Ni_2P.

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[3] Comets and the rings of Saturn ought now to be considered as consisting of an accumulation of such meteoric cosmic particles. Perhaps the part played by these minute bodies scattered throughout space is much more important in the formation of the largest celestial bodies than has hitherto been imagined. The investigation of this branch of astronomy, due to Schiaparelli, has a bearing on the whole of natural science.

The question arises as to why the iron in meteorites is in a free state, whilst on earth it is in a state of combination. Does not this tend to show that the condition of our globe is very different from that of the rest? My answer to this question has been already given in Volume I. p. 377, Note 57. It is my opinion that inside the earth there is a mass similar in composition to meteorites—that is, containing rocky matter and metallic iron, partly carburetted. In conclusion, I consider it will not be out of place to add the following explanations. According to the theory of the distribution of pressures (see my treatise, *On Barometrical Levelling*, 1876, pages 48 *et seq.*) in an atmosphere of mixed gases, it follows that two gases, whose densities are d and d_1, and whose relative quantities or partial pressures at a certain distance from the centre of gravity are h and h_1, will, when at a greater distance from the centre of attraction, present a different ratio of their masses $x : x_1$—that is, of their partial pressures—which may be found by the equation $d_1(\log h - \log x) = d(\log h_1 - \log x_1)$. If, for instance, $d : d_1 = 2 : 1$, and $h = h_1$ (that is to say, the masses are equal at the lower height) $= 1000$, then when $x = 10$ the magnitude of x_1 will not be 10 (*i.e.* the mass of a gas at a higher level whose density $= 1$ will not be equal to the mass of a gas whose density $= 2$, as was the case at a lower level), but much greater—namely, $x_1 = 100$—that is, the lighter gas will predominate over a heavier one at a higher level. Therefore, when the whole mass of the earth was in a state of vapour, the substances having a greater vapour density accumulated about the centre and those with a lesser vapour density at the surface. And as the vapour densities depend on the atomic and molecular weights, those substances which have small atomic and molecular weights ought to have accumulated at the surface, and those with high atomic and molecular weights, which are the least volatile and the easiest to condense, at the centre. Thus it becomes apparent why such light elements as hydrogen, carbon, nitrogen, oxygen, sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, and their compounds predominate at the surface and largely form the earth's crust. There is also now much iron in the sun, as spectrum analysis shows, and therefore it must have entered into the composition of the earth and other planets, but would have accumulated at the centre, because the density of its vapour is certainly large and it easily condenses. There was also oxygen near the centre of the earth, but not sufficient to combine with the iron. The former, as a much lighter element, principally accumulated at the surface, where we at the present time find all oxidised compounds and even a remnant of free oxygen. This gives the possibility not only of explaining in accordance with cosmogonic theories the predominance of oxygen compounds on the surface of the earth, with the occurrence of unoxidised iron in the interior of the earth and in meteorites, but also of understanding why the density of the whole earth (over 5) is far greater than that of the rocks (about 2.5) composing its crust. And if all the preceding arguments and theories (for instance the supposition that the sun, earth, and all the planets were formed of an elementary homogeneous mass, formerly composed of vapours and gases) be true, it must be admitted that the interior of the earth and other planets contains metallic (unoxidised) iron, which, however, is only found on the surface as aerolites. And then assuming that aerolites are the fragments of planets which have crumbled to pieces so to say during cooling (this has been held to be the case by astronomers, judging from the paths the doctrine concerning meteorites, and therefore the fact of their containing rocky (siliceous) matter and metallic iron shows that outside the earth the elements and their aggregation are in some degree the same as upon the earth itself.

The most widely diffused terrestrial compound of iron is iron bisulphide, FeS_2, or *iron pyrites*. It occurs in formations of both aqueous and igneous origin, and sometimes in enormous masses. It is a substance having a greyish-yellow colour, with a metallic lustre, and a specific gravity of 5·0; it crystallises in the regular system.[2 bis]

The oxides are the principal ores used for producing metallic iron. The majority of the ores contain ferric oxide, Fe_2O_3, either in a free state or combined with water, or else in combination with ferrous oxide, FeO The species and varieties of iron ores are numerous and diverse. Ferric oxide in a separate form appears sometimes as crystals of the rhombohedric system, having a metallic lustre and greyish steel colour; they are brittle, and form a red powder, specific gravity about 5·25. Ferric oxide in type of oxidation and properties resembles alumina; it is, however, although with difficulty, soluble in acids even when anhydrous. The crystalline oxide bears the name of *specular iron ore*, but ferric oxide most often occurs in a non-crystalline form, in masses having a red fracture, and is then known as *red hæmatite*. In this form, however, it is rather a rare ore, and is principally found in veins. The hydrates of ferric oxide, ferric hydroxides,[3] are most

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of aerolites), it is readily understood why they should be composed of metallic iron, and this would explain its occurrence in the depths of the earth, which we assumed as the basis of our theory of the formation of naphtha (Chapter VIII., Notes 57–60).

[2 bis] Immense deposits of iron pyrites are known in various parts of Russia. On the river Mata, near Borovitsi, thousands of tons are yearly collected from the detritus of the neighbouring rocks. In the Governments of Toula, Riazan, and in the Donets district continuous layers of pyrites occur among the coal seams. Very thick beds of pyrites are also known in many parts of the Caucasus. But the deposits of the Urals are particularly vast, and have been worked for a long time. Amongst these I will only indicate the deposits on the Soymonsky estate near the Kishteimsky works; the Kaletinsky deposits near the Verhny Isetsky works (containing 1-2 p.c. Cu); on the banks of the river Kouchaivi near Koushva (3·5 p.c. Cu), and the deposits near the Bogoslovsky works (3-5 p.c. Cu). Iron pyrites (especially that containing copper which is extracted after roasting) is now chiefly employed for roasting, as a source of SO_2 for the manufacture of chamber sulphuric acid (Vol. I p. 291), but the remaining oxide of iron is perfectly suitable for smelting into pig iron, although it gives a sulphurous pig iron (the sulphur may be easily removed by subsequent treatment, especially with the aid of ferro manganese in Bessemer's process). The great technical importance of iron pyrites leads to its sometimes being imported from great distances; for instance, into England from Spain. Besides which, when heated in closed retorts FeS_2 gives sulphur, and if allowed to oxidise in damp air, green vitriol, $FeSO_4$.

[3] The hydrated ferric oxide is found in nature in a dual form It is somewhat rarely met with in the form of a crystalline mineral called *göthite*, whose specific gravity is 4·4

often found in aqueous or stratified formations, and are known as *brown hæmatites*; they generally have a brown colour, form a yellowish-brown powder, and have no metallic lustre but an earthy appearance. They easily dissolve in acids and diffuse through other formations, especially clays (for instance, ochre); they sometimes occur in reniform and similar masses, evidently of aqueous origin. Such are, for instance, the so-called bog or lake and peat ores found at the bottom of marshes and lakes, and also under and in peat beds. This ore is formed from water containing ferrous carbonate in solution, which, after absorbing oxygen, deposits ferric hydroxide. In rivers and springs, iron is found in solution as ferrous carbonate through the agency of carbonic acid: hence the existence of chalybeate springs containing $FeCO_3$. This ferrous carbonate, or *siderite*, is either found as a non-crystalline product of evidently aqueous origin, or as a crystalline spar called *spathic iron ore*. The reniform deposits of the former are most remarkable; they are called spherosiderites, and sometimes form whole strata in the jurassic and carboniferous formations. *Magnetic iron ore*, $Fe_3O_4 = FeO,Fe_2O_3$, in virtue of its purity and practical uses, is a very important ore; it is a compound of the ferrous and ferric oxides, is naturally magnetic, has a specific gravity of 5·1, crystallises in well formed crystals of the regular system, is with difficulty soluble in acids, and sometimes forms enormous masses, as, for instance, Mount Blagodat in the Ural. However, in most cases—for instance, at Korsak-Mogila (to the north of Berdiansk and Nogaisk, near the Sea of Azov), or at Krivoi Rog (to the west of Ekaterinoslav)—the magnetic iron ore is mixed with other iron ores. In the Urals, the Caucasus (without mentioning Siberia), and in the districts adjoining the basin of the Don, Russia possesses the richest iron ores in the world. To the south of Moscow, in the Governments of Toula and Nijni-novgorod, in the Olonetz district, and in the Government of Orloffsky (near Zinovieff in the district of Kromsky), and in many other places, there are likewise abundant supplies of iron ores amongst the deposited aqueous formations; the siderite of Orloffsky, for instance, is distinguished by its great purity.[4]

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and composition $Fe_2H_2O_4$, or $FeHO_2$—that is, one of oxide of iron to one of water, Fe_2O_3,H_2O; frequently found as brown ironstone, forming a dense mass of fibrous, reniform deposits containing $2Fe_2O_3,3H_2O$—that is, having a composition $Fe_4H_6O_9$. In bog ore and other similar ores we most often find a mixture of this hydrated ferric oxide with clay and other impurities. The specific gravity of such formations is rarely as high as 4·0.

[4] The ores of iron, similarly to all substances extracted from veins and deposits, are worked according to mining practice by means of vertical, horizontal, or inclined shafts which reach and penetrate the veins and strata containing the ore deposits. The mass of ore excavated is raised to the surface, then sorted either by hand or else in

Iron is also found in the form of various other compounds—for instance, in certain silicates, and also in some phosphates; but these forms are comparatively rare in nature in a pure state, and have not the industrial importance of those natural compounds of iron previously mentioned. In small quantities iron enters into the composition of every kind of *soil* and all rocky formations. As ferrous oxide, FeO, is isomorphous with magnesia, and ferric oxide, Fe_2O_3, with alumina, isomorphous substitution is possible here, and hence minerals are not unfrequently found in which the quantity of iron varies considerably; such, for instance, are pyroxene, amphibole, certain varieties of mica, &c. Although much iron oxide is deleterious to the growth of vegetation, still plants do not flourish without iron; it enters as an indispensable component into the composition of all higher *organisms*; in the ash of plants we always find more or less of its compounds. It also occurs in blood, and forms one of the colouring matters in it; 100 parts of the blood of the highest organisms contain about 0·05 of iron.

The *reduction* of the ores of iron into metallic iron is in principle very simple, because when the oxides of iron are strongly heated with charcoal, hydrogen, carbonic oxide, and other reducing agents,[5] they easily give metallic iron. But the matter is rendered more

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special sorting apparatus (generally acting with water to wash the ore), and is subjected to roasting and other treatment. In every case the ore contains foreign matter. In the extraction of iron, which is one of the cheapest metals, the dressing of an ore is in most cases unprofitable, and only ores rich in metal are worked—namely, those containing at least 20 p.c. It is often profitable to transport very rich and pure ores (with as much as 70 p.c. of iron) from long distances. The details concerning the working and extraction of metals will be found in special treatises on metallurgy and mining.

[5] The reduction of iron oxides by hydrogen belongs to the order of reversible reactions (Chapter II.), and is therefore determined by a limit which is here expressed by the attainment of the same pressure as in the case where hydrogen acts on iron oxides, and as in the case where (at the same temperature) water is decomposed by metallic iron. The calculations referring to this matter were made by Henri Sainte-Claire Deville (1870). Spongy iron was placed in a tube having a temperature t, one end of which was connected with a vessel containing water at 0° (vapour tension = 4·6 mm.) and the other end with a mercury pump and pressure gauge which determined the limiting tension attained by the dry hydrogen p (subtracting the tension of the water vapour from the tension observed). A tube was then taken containing an excess of iron oxide. It was filled with hydrogen, and the tension p_1 observed of the residual hydrogen when the water was condensed at 0°.

t = 200°	440°	860°	1040°
p = 95·9	25·8	12·8	9·2 mm.
p_1 = —	—	12·8	9·4 mm.

The equality of the pressure (tension) of the hydrogen in the two cases is evident. The hydrogen here behaves like the vapour of iron or of its oxide.

By taking ferric oxide, Fe_2O_3, Moissan observed that at 350° it passed into magnetic oxide, Fe_3O_4, at 500° into ferrous oxide, FeO, and at 600° into metallic iron. Wright and Luff (1878), whilst investigating the reduction of oxides, found that (a) the temperature of reaction depends on the condition of the oxide taken—for instance difficult by the fact that the iron does not melt at the heat developed by the combustion of the charcoal, and therefore it does not separate from those mechanically mixed impurities which are found in the iron ore. This is obviated by the following very remarkable property of iron: at a high temperature it is capable of combining with a small quantity (from 2 to 5 p.c.) of carbon, and then forms *cast iron*, which easily *melts* in the heat developed by the combustion of charcoal in air. For this reason metallic iron is not obtained directly from the ore, but is only formed after the further treatment of the cast iron; the first product extracted from the ore being cast iron. The fused mass disposes itself in the furnace below the slag—that is, the impurities of the ore fused by the heat of the furnace. If these impurities did not fuse they would block up the furnace in which the ore was being smelted, and the continuous smelting of the cast iron would not be possible;[6] it would be necessary periodically to cool the furnace and heat it up again, which means a wasteful expenditure of fuel, and hence in the production of cast iron, the object in view is to obtain all the earthy impurities of the ore in the shape of a fused mass or slag. Only in rare cases does the ore itself form a mass which fuses at the temperature employed, and these cases are objectionable if much iron oxide is carried away in the slag. The impurities of the ores most often consist of certain mixtures—for instance, a mixture of clay and sand, or a mixture of limestone and clay, or quartz, &c. These

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precipitated ferric oxide is reduced by hydrogen at 85°, that obtained by oxidising the metal or from its nitrate at 175°; (*b*) when other conditions are the same the reduction by carbonic oxide commences earlier than that by hydrogen, and the reduction by hydrogen still earlier than that by charcoal; (*c*) the reduction is effected with greater facility when a greater quantity of heat is evolved during the reaction. Ferric oxide obtained by heating ferrous sulphate to a red heat begins to be reduced by carbonic oxide at 202°, by hydrogen at 260°, by charcoal at 430°, whilst for magnetic oxide, Fe_3O_4, the temperatures are 200°, 290°, and 450° respectively.

[6] The primitive methods of iron manufacture were conducted by intermittent processes in hearths resembling smiths' fires. As evidenced by the uninterrupted action of the steam boiler, or the process of lime burning, and the continuous preparation and condensation of sulphuric acid or the uninterrupted smelting of iron, every industrial process becomes increasingly profitable and complete under the condition of the continuous action, as far as possible, of all agencies concerned in the production. This continuous method of production is the first condition for the profitable production on the large scale of nearly all industrial products. This method lessens the cost of labour, simplifies the supervision of the work, renders the product uniform, and frequently introduces a very great economy in the expenditure of fuel and at the same time presents the simplicity and perfection of an equilibrated system. Hence every manufacturing operation should be a continuous one, and the manufacture of pig iron and sulphuric acid, which have long since become so, may be taken as examples in many respects. A study of these two manufactures should form the commencement of an acquaintance with all the contemporary methods of manufacturing both from a technical and economical point of view.

impurities do not separate of themselves, or do not fuse. The difficulty of the industry lies in forming an easily-fusible slag, into which the whole of the foreign matter of the ore would pass and flow down to the bottom of the furnace above the heavier cast iron. This is effected by mixing certain *fluxes* with the ore and charcoal. A flux is a substance which, when mixed with the foreign matter of the ore, forms a fusible vitreous mass or slag. The flux used for silica is limestone with clay; for limestone a definite quantity of silica is used, the best procedure having been arrived at by experiment and by long practice in iron smelting and other metallurgical processes.[7]

Thus the following materials have to be introduced into the furnace where the smelting of the iron ore is carried on: (1) the iron ore, composed of oxide of iron and foreign matter; (2) the flux required to form a fusible slag with the foreign matter; (3) the carbon which is necessary (*a*) for reducing, (*b*) for combining with the reduced iron to form cast iron, (*c*) principally for the purpose of combustion and the heat generated thereby, necessary not only for reducing the iron and transforming it into cast iron, but also for melting the slag, as well as the cast iron—and (4) the air necessary for the combustion of the charcoal. The air is introduced after a preparatory heating in order to economise fuel and to obtain the highest temperature. The air is forced in under pressure by means of a special blast arrangement. This permits of an exact regulation of the heat and rate of smelting. All these component parts necessary for the smelting of iron must be contained in a vertical, that is, *shaft furnace*, which at the base must have a receptacle for the accumulation of the slag and cast iron formed, in order that the operation may proceed without interruption. The walls of such a furnace ought to be built of fireproof materials if it be designed to serve for the continuous production of cast iron by charging the ore, fuel, and flux into the mouth of the furnace, forcing a blast of air into the lower part, and running out the molten iron and slag from below. The whole operation is conducted in furnaces known as *blast furnaces.* The annexed illustration, fig. 93 (which is taken by kind permission from Thorpe's Dictionary of Applied Chemistry), represents the vertical section of such a furnace. These furnaces are generally of large dimensions—varying from 50 to 90 feet in height. They are sometimes built against rising ground in order to afford easy access to the top where the ore, flux, and charcoal or coke are charged.[8]

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[7] The composition of slag suitable for iron smelting most often approaches the following: 50 to 60 p.c. SiO_2, 5 to 20 Al_2O_3, the rest of the mass consisting of MgO, CaO, MnO, FeO. Thus the most fusible slag (according to the observations of Bodeman) contains the alloy $Al_2O_3,4CaO,7SiO_2$. On altering the quantity of magnesia and lime, and especially of the alkalis (which increases the fusibility) and of silica (which decreases it), the temperature of fusion changes with the relation between the total quantity of oxygen and that in the silica. Slags of the composition RO,SiO_2 are easily fusible, have a vitreous appearance, and are very common. Basic slags approach the composition $2RO,SiO_2$. Hence, knowing the composition and quantity of the foreign matter in the ore, it is at once easy to find the quantity and quality of the flux which must be added to form a suitable slag. The smelting of iron is rendered more complex by the fact that the silica, SiO_2, which enters into the slag and fluxes is capable of forming a slag with the iron oxides. In order that the least quantity of iron may pass into the slag, it is necessary for it to be reduced before the temperature is attained at which the slags are formed (about 1000°), which is effected by reducing the iron, not with charcoal itself, but with carbonic oxide. From this it will be understood how the progress of the whole treatment may be judged by the properties of the slags. Details of this complicated and well-studied subject will be found in works on metallurgy.

[8] The section of a blast furnace is represented by two truncated cones joined at their bases, the upper cone being longer than the lower one; the lower cone is terminated by the hearth, or almost cylindrical cavity in which the cast iron and slag collect, one side being provided with apertures for drawing off the iron and slag. The air is blown into the blast furnace through special pipes, situated over the hearth, as shown in the section. The air previously passes through a series of cast iron pipes, heated by the combustion of the carbonic oxide obtained from the upper parts of the furnace, where it is formed as in a 'gas producer.' The blast furnace acts continuously until it is worn out; the iron is tapped off twice a day, and the furnace is allowed to cool a little from time to time so as not to be spoilt by the increasing heat, and to enable it to withstand long usage.

Blast furnaces worked with charcoal fuel are not so high, and in general give a smaller yield than those using coke, because the latter are worked with heavier charges than those in which charcoal is employed. Coke furnaces yield 20,000 tons and over of pig iron a year. In the United States there are blast furnaces 30 metres high, and upwards of 600 cubic metres capacity, yielding as much as 130,000 tons of pig iron, requiring a blast of about 750 cubic metres of air per minute, heated to 600°, and consuming about 0·85 part of coke per 1 part of pig iron produced. At the present time the world produces as much as 30 million tons of pig iron a year, about $\frac{3}{5}$ of which is converted into wrought iron and steel. The chief producers are the United States (about 10 million tons a year) and England (about 9 million tons a year). Russia yields about 1½ million tons a year. The world's production has doubled during the last 20 years, and in this respect the United States have outrun all other countries. The reason of this increase of production must be looked for in the increased demand for iron and steel for railway purposes, for structures (especially ship building), and in the fact that (*a*) the cost of pig iron has fallen, thanks to the erection of large furnaces and a fuller study of the processes taking place in them, and (*b*) that every kind of iron ore (even sulphurous and phosphoric) can now be converted into a homogeneous steel.

In order to more thoroughly grasp the chemical process which takes place in blast furnaces, it is necessary to follow the course of the material charged in at the top and of the air passing through the furnace. From 80 to 200 parts of carbon are expended on 100 parts of iron. The ore, flux, and coke are charged into the top of the furnace, in layers, as the cast iron is formed in the lower parts and flowing down to the bottom causes the whole contents of the furnace to subside, thus forming an empty space at the top, which is again filled up with the afore-mentioned mixture. During its downward course this mixture is subjected to increasing heat. This rise of temperature first drives off the moisture of the ore mixture, and then leads to the formation of the products of the dry distillation of coal or charcoal. Little by little the subsiding mass attains a temperature at which the heated carbon reacts with the carbonic anhydride passing upwards through the furnace and transforms it into carbonic oxide. This is the reason why carbonic anhydride is not evolved from the furnace, but only carbonic oxide. As regards the ore itself, on being heated to about 600° to 800° it is reduced at the expense of the carbonic oxide ascending the furnace, and formed by the contact of

The *cast iron* formed in blast furnaces is not always of the same quality. When slowly cooled it is soft, has a grey colour, and is not

the carbonic anhydride with the incandescent charcoal, so that the reduction in the blast furnace is without doubt brought about *by* the formation and decomposition of *carbonic oxide* and not by carbon itself—thus, $Fe_2O_3+3CO=Fe_2+3CO_2$. The reduced iron, on further subsidence and contact with carbon, forms cast iron, which flows to the bottom of the furnace. In those lower layers, where the temperature is highest (about 1,800°), the foreign matter of the ore finally forms slag, which also is fusible, with the aid of fluxes. The air blown in from below, through the so-called *tuyeres*, encounters carbon in the lower layers of the furnace, and burns it, converting it into carbonic anhydride It is evident that this develops the highest temperature in these lower layers of the furnace, because here the combustion of the carbon is effected by heated and compressed air. This is very essential, for it is by virtue of this high temperature that the process of forming the slag and of forming and fusing the cast iron are effected

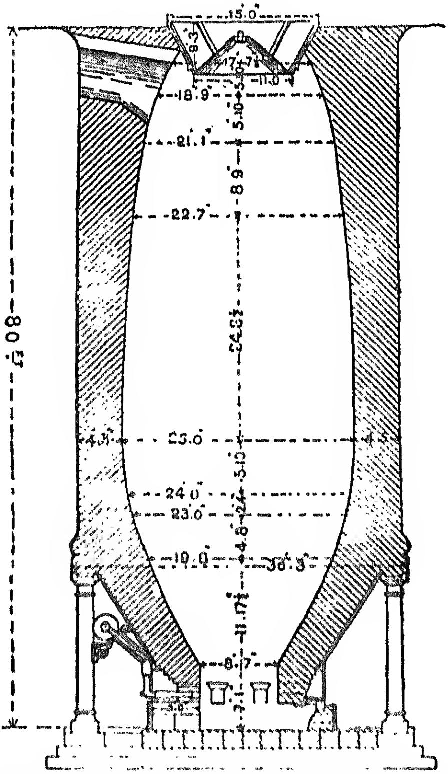

FIG. 93.—Vertical section of a modern Cleveland blast furnace capable of producing 300 to 1,000 tons of pig iron weekly. The outer casing is of riveted iron plates, the furnace being lined with refractory fire brick. It is closed at the top by a 'cup and cone' arrangement, by means of which the charge can be fed into the furnace at suitable intervals by lowering the moveable cone.

completely soluble in acids. When treated with acids a residue of graphite remains; it is known as *grey* or soft cast iron. This is the general form of the ordinary cast iron used for casting various objects, because in this state it is not so brittle as in the shape of *white cast iron*, which does not leave particles of graphite when dissolved, but yields its carbon in the form of hydrocarbons. This white cast iron is characterised by its whitish-grey colour, dull lustre, the crystalline structure of its fracture (more homogeneous than that of grey iron), and such hardness that a file will hardly cut it. When white cast iron is produced (from manganese ore) at high temperatures (and with an excess of lime), and containing little sulphur and silica but a considerable amount of carbon (as much as 5 p.c.), it acquires a coarse crystalline structure which increases in proportion to the amount of manganese, and it is then known under the name of 'spiegeleisen' (and 'ferromanganese').[8]

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simultaneously in these lower portions of the furnace. The carbonic acid formed in these parts rises higher, encounters incandescent carbon, and forms with it carbonic oxide. This heated carbonic oxide acts as a reducing agent on the iron ore, and is reconverted by it into carbonic anhydride; this gas meets with more carbon, and again forms carbonic oxide, which again acts as a reducing agent. The final transformation of the carbonic anhydride into carbonic oxide is effected in those parts of the furnace where the reduction of the oxides of iron does not take place, but where the temperature is still high enough to reduce the carbonic anhydride. The ascending mixture of carbonic oxide and nitrogen, CO_2, &c., is then withdrawn through special lateral apertures formed in the upper cold parts of the furnace walls, and is conducted through pipes to those stoves which are used for heating the air, and also sometimes into other furnaces used for the further processes of iron manufacture. The fuel of blast furnaces consists of wood charcoal (this is the most expensive material, but the pig iron produced is the purest, because charcoal does not contain any sulphur, while coke does), anthracite (for instance, in Pennsylvania, and in Russia at Pastouhoff's works in the Don district), coke, coal, and even wood and peat. It must be borne in mind that the utilisation of naphtha and naphtha refuse would probably give very profitable results in metallurgical processes.

The process just described is accompanied by a series of other processes. Thus, for instance, in the blast furnace a considerable quantity of cyanogen compounds are formed. This takes place because the nitrogen of the air blast comes into contact with incandescent carbon and various alkaline matters contained in the foreign matter of the ores. A considerable quantity of potassium cyanide is formed when wood charcoal is employed for iron smelting, as its ash is rich in potash.

[8] The specific gravity of white cast iron is about 7.5. Grey cast iron has a much lower specific gravity, namely, 7.0. Grey cast iron generally contains less manganese and more silica than white; but both contain from 2 to 3 p.c. of carbon. The difference between the varieties of cast iron depends on the condition of the carbon which enters into the composition of the iron. In white cast iron the carbon is in combination with the iron—in all probability, as the compound CFe_3 (Abel and Osmond and others extracted this compound, which is sometimes called 'carbide,' from tempered steel, which stands to unannealed steel as white cast iron does to grey), but perhaps in the state of an indefinite chemical compound resembling a solution. In any case the compound of the iron and carbon in white cast iron is chemically very unstable, because when slowly cooled it decomposes, with separation of graphite, just as a solution when slowly cooled

Cast iron is a material which is either suitable for direct application for casting in moulds or else for working up into *wrought iron* and *steel*. The latter principally differ from cast iron in their containing less carbon—thus, steel contains from 1 p.c. to 0·5 p.c. of carbon and far less silicon and manganese than cast iron; wrought iron does not generally contain more than 0·25 p.c. of carbon and not more than 0·25 p.c. of the other impurities. Thus the essence of the working up of cast iron into steel and wrought iron consists in the removal of the greater part of the carbon and other elements, S, P, Mn, Si, &c. This is effected by means of oxidation, because the oxygen of the atmosphere, oxidising the iron at a high temperature, forms solid oxides with it; and the latter, coming into contact with the carbon contained in the cast iron, are deoxidised, forming wrought iron and carbonic oxide, which is evolved from the mass in a gaseous form. It is evident that the oxidation must be carried on with a molten mass in a state of agitation, so that the oxygen of the air may be brought into contact with the whole mass of carbon contained in the cast iron, or else the operation is effected by means of the addition of oxygen compounds of iron (oxides, ores, as in Martin's process). Cast iron melts much more easily than wrought iron and steel, and, therefore, as the carbon separates, the mass in the furnace (in puddling) or hearth (in the bloomery process) becomes more and more solid; moreover the degree of hardness forms, to a certain extent, a measure of the amount of carbon separated, and the operation may terminate either in the formation of steel or wrought iron.[10] In any case, the iron used for industrial pur-

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yields a portion of the substance dissolved. The separation of carbon in the form of graphite on the conversion of white cast iron into grey is never complete, however slowly the separation be carried on; part of the carbon remains in combination with the iron in the same state in which it exists in white cast iron. Hence when grey cast iron is treated with acids, the whole of the carbon does not remain in the form of graphite, but a part of it is separated as hydrocarbons, which proves the existence of chemically-combined carbon in grey cast iron. It is sufficient to re-melt grey cast iron and to cool it quickly to transform it into white cast iron. It is not carbon alone that influences the properties of cast iron; when it contains a considerable amount of sulphur, cast iron remains white even after having been slowly cooled. The same is observed in cast iron very rich in manganese (5 to 7 p.c.), and in this latter case the fracture is very distinctly crystalline and brilliant. When cast iron contains a large amount of manganese, the quantity of carbon may also be increased. Crystalline varieties of cast iron rich in manganese are in practice called ferro-manganese (p. 310), and are prepared for the Bessemer process. Grey cast iron not having an uniform structure is much more liable to various changes than dense and thoroughly uniform white cast iron, and the latter oxidises much more slowly in air than the former. White cast iron is not only used for conversion into wrought iron and steel, but also in those cases where great hardness is required, although it be accompanied by a certain brittleness, for instance, for making rollers, plough-shares, &c.

[10] This direct process of separating the carbon from cast iron is termed *puddling*. It is conducted in reverberatory furnaces. The cast iron is placed on the bed of the furnace and melted; through a special aperture, the puddler stirs up the oxidising mass

poses contains impurities. *Chemically pure iron* may be obtained by precipitating iron from a solution (a mixture of ferrous sulphate with

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of cast iron, pressing the oxides into the molten iron. This resembles kneading dough, and the process introduced in England became known as puddling. It is evident that the puddled mass, or bloom, is a heterogeneous substance obtained by mixing, and hence one part of the mass will still be rich in carbon, another will be poor, some parts will contain oxide not reduced, &c. The further treatment of the puddled mass consists in hammering and drawing it out into flat pieces, which on being hammered become more homogeneous, and when several pieces are welded together and again hammered out a still more homogeneous mass is obtained. The quality of the steel and iron thus formed depends principally on their uniformity. The want of uniformity depends on the oxides remaining inside the mass, and on the variable distribution of the carbon throughout the mass. In order to obtain a more homogeneous metal for manufacturing articles out of steel, it is drawn into thin rods, which are tied together in bundles and then again hammered out. As an example of what may be attained in this direction, imitation Damascus steel may be cited; it consists of twisted and plaited wire, which is then hammered into a dense mass. (Real damascened wootz steel may be made by melting a mixture of the best iron with graphite ($\frac{1}{10}$) and iron rust; the article is then corroded with acid, and the carbon remains in the form of a pattern.)

Steel and wrought iron are manufactured from cast iron by puddling. They are, however, obtained not only by this method but also by the *bloomery process*, which is carried out in a fire similar to a blacksmith's forge, fed with charcoal and provided with a blast; a pig of cast iron is gradually pushed into the fire, and portions of it melt and fall to the bottom of the hearth, coming into contact with an air blast, and are thus oxidised. The bloom thus formed is then squeezed and hammered. It is evident that this process is only available when the charcoal used in the fire does not contain any foreign matter which might injure the quality of the iron or steel—for instance, sulphur or phosphorus—and therefore only wood charcoal may be used with impunity, from which it follows that this process can only be carried on where the manufacture of iron can be conducted with this fuel. Coal and coke contain the above-mentioned impurities, and would therefore produce iron of a brittle nature, and thus it would be necessary to have recourse to puddling, where the fuel is burnt on a special hearth, separate from the cast iron, whereby the impurities of the fuel do not come into contact with it. The manufacture of steel from cast iron may also be conducted in fires, but, in addition to this, it is also now prepared by many other methods. One of the long known processes is called *cementation*, by which steel is prepared from wrought iron but not from cast iron. For this process strips of iron are heated red hot for a considerable time whilst immersed in powdered charcoal; during this operation the iron at the surface combines with the charcoal, which however does not penetrate; after this the iron strips are re-forged, drawn out again, and cemented anew, repeating this process until a steel of the desired quality is formed—that is, containing the requisite proportion of carbon. The *Bessemer process* occupies the first rank among the newer methods (since 1856); it is so called from the name of its inventor. This process consists in running melted cast iron into converters (holding about 6 tons of cast iron)—that is, egg-shaped receivers, fig. 94, capable of revolving on trunnions (in order to charge in the cast iron and discharge the steel), and forcing a stream of air through small apertures at a considerable pressure. Combustion of the iron and carbon at an elevated temperature then takes place, resulting from the bubbles of oxygen thus penetrating the mass of the cast iron. The carbon, however, burns to a greater extent than the iron, and therefore a mass is obtained which is much poorer in carbon than cast iron. As the combustion proceeds very rapidly in the mass of metal, the temperature rises to such an extent that even the wrought iron which may be *formed* remains in a molten condition, whilst the steel, being more fusible than the wrought iron, remains very liquid. In half an hour the mass is ready. The purest possible cast iron is used in the Bessemer magnesium sulphate or ammonium chloride) by the prolonged action of a feeble galvanic current; the iron may be then obtained as a dense

process, because sulphur and phosphorus do not burn out like carbon, silicon, and manganese.

The presence of manganese enables the sulphur to be removed with the slag, and the presence of lime or magnesia, which are introduced into the lining of the converter, facilitates the removal of the phosphorus. This basic Bessemer process, or *Thomas Gilchrist process*, introduced about 1880, enables ores containing a considerable amount of phosphorus, which had hitherto only been used for cast iron, to be used for making wrought iron and steel. Naturally the greatest uniformity will be obtained by re-melting the metal. Steel is re-melted in small wind furnaces, in masses not exceeding 30 kilos; a liquid metal is formed, which may be cast in moulds. A mixture of wrought and cast iron is often used for making cast steel (the addition of a small amount of metallic Al improves the homogeneity of the castings, by facilitating the passage of the impurities into slag). Large steel castings are made by simultaneous fusion in several furnaces and crucibles; in this way, castings up to 80 tons or more, such as large ordnance, may be made. This molten, and therefore homogeneous, steel is called *cast steel*. Of late years the *Martin's process* for the manufacture of steel has come largely into use; it was invented in France about 1860, and with the use of regenerative furnaces it enables large quantities of cast steel to be made at a time. It is based on the melting of cast iron with iron oxides and iron itself—for instance, pure ores, scrap, &c. There the carbon of the cast iron and the oxygen of the oxide form carbonic oxide, and the carbon therefore burns out, and thus cast steel is obtained from cast iron, providing, naturally, that there is a requisite proportion and corresponding degree of heat. The advantage of this

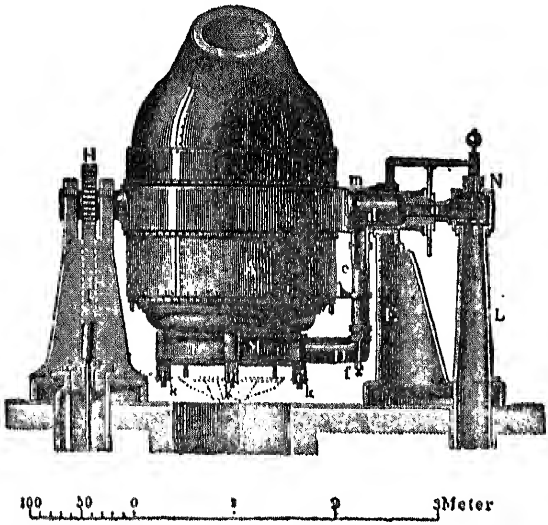

FIG. 94.—Bessemer converter, constructed of iron plate and lined with ganister. The air is carried by the tubes, L, O, D to the bottom, M, from which it passes by a number of holes into the converter. The converter is rotated on the trunnion *d* by means of the rack and pinion H, when it is required either to receive molten cast iron from the melting furnaces or to pour out the steel.

mass. This method, proposed by Böttcher and applied by Klein, gives, as R. Lenz showed, iron containing occluded hydrogen, which is dis-

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process is that not only do the carbon, silicon, and manganese, but also a great part of the sulphur and phosphorus of the cast iron burn out at the expense of the oxygen of the iron oxides. During the last decade the manufacture of steel and its application for rails, armour plate, guns, boilers, &c., has developed to an enormous extent, thanks to the invention of cheap processes for the manufacture of large masses of homogeneous cast steel. Wrought iron may also be melted, but the heat of a blast furnace is insufficient for this. It easily melts in the oxyhydrogen flame. It may be obtained in a molten state directly from cast iron, if the latter be melted with nitre and sufficiently stirred up. Considerable oxidation then takes place inside the mass of cast iron, and the temperature rises to such an extent that the wrought iron formed remains liquid. A method is also known for obtaining wrought iron directly from rich iron ores by the action of carbonic oxide; the wrought iron is then formed as a spongy mass (which forms an excellent filter for purifying water), and may be worked up into wrought iron or steel either by forging or by dissolving in molten cast iron.

Everybody is more or less familiar with the *difference in the properties of steel and wrought iron*. Iron is remarkable for its softness, pliability, and small elasticity, whilst steel may be characterised by its capability of attaining elasticity and hardness if it be cooled suddenly after having been heated to a definite temperature, or, as it is termed, *tempered*. But if tempered steel be re-heated and slowly cooled, it becomes as soft as wrought iron, and can then be cut with the file and forged, and in general can be made to assume any shape, like wrought iron. In this soft condition it is called *annealed steel*. The transition from tempered to annealed steel thus takes place in a similar way to the transition from white to grey cast iron. Steel, when homogeneous, has considerable lustre, and such a fine granular structure that it takes a very high polish. Its fracture clearly shows the granular nature of its structure. The possibility of tempering steel enables it to be used for making all kinds of cutting instruments, because annealed steel can be forged, turned, drawn (under rollers, for instance, for making rails, bars, &c.), filed, &c., and it may then be tempered, ground and polished. The method and temperature of tempering and annealing steel determine its hardness and other qualities. Steel is generally tempered to the required degree of hardness in the following manner. It is first strongly heated (for instance, up to 600°), and then plunged into water—that is, hardened by rapid cooling (it then becomes as brittle as glass). It is then heated until the surface assumes a definite colour, and finally cooled either quickly or slowly. When steel is heated up to 220°, its surface acquires a yellow colour (surgical instruments), it first of all becomes straw-coloured (razors, &c.), and then gold-coloured; then at a temperature of 250° it becomes brown (scissors), then red, then light blue at 285° (springs), then indigo at 300° (files), and finally sea green at about 340°. These colours are only the tints of thin films, like the hues of soap bubbles, and appear on the steel because a thin layer of oxides is formed over its surface. Steel rusts more slowly than wrought iron, and is more soluble in acids than cast iron, but less so than wrought iron. Its specific gravity is about 7·6 to 7·9.

As regards the formation of steel, it was a long time before the process of cementation was thoroughly understood, because in this case infusible charcoal permeates unfused wrought iron. Caron showed that this permeation depends on the fact that the charcoal used in the process contains alkalis, which, in the presence of the nitrogen of the air, form metallic cyanides; these being volatile and fusible, permeate the iron, and, giving up their carbon to it, serve as the material for the formation of steel. This explanation is confirmed by the fact that charcoal without alkalis or without nitrogen will not cement iron. The charcoal used for cementation acts badly when used over again, as it has lost alkali. The very volatile ammonium cyanide easily conduces to the formation of steel. Although steel is also formed by the action of cyanogen compounds, nevertheless it does not contain more nitrogen than cast or wrought iron (0·01 p.c.), and engaged on heating. This galvanic deposition of iron is used for making galvanoplastic *clichés*, which are distinguished for their great

those latter contain it because their ores contain titanium, which combines directly with nitrogen. Hence the part played by nitrogen in steel is but an insignificant one. It may be useful here to add some information taken from Caron's treatise concerning the influence of foreign matter on the quality of steel. The principal properties of steel are those of tempering and annealing. The compounds of iron with silicon and boron have not those properties. They are more stable than the carbon compound, and this latter is capable of changing its properties; because the carbon in it either enters into combination or else is disengaged, which determines the condition of hardness or softness of steel, as in white and grey cast iron. When slowly cooled, steel splits up into a mixture of soft and carburetted iron; but, nevertheless, the carbon does not separate from the iron. If such steel be again heated, it forms a uniform compound, and hardens when rapidly cooled. If the same steel as before be taken and heated a long time, then, after being slowly cooled, it becomes much more soluble in acid, and leaves a residue of pure carbon. This shows that the combination between the carbon and iron in steel becomes destroyed when subjected to heat, and the steel becomes iron mixed with carbon. Such *burnt* steel cannot be tempered, but may be corrected by continued forging in a heated condition, which has the effect of redistributing the carbon equally throughout the whole mass. After the forging, if the iron is pure and the carbon has not been burnt out, steel is again formed, which may be tempered. If steel be repeatedly or strongly heated, it becomes burnt through and cannot be tempered or annealed; the carbon separates from the iron, and this is effected more easily if the steel contains other impurities which are capable of forming stable combinations with iron, such as silicon, sulphur, or phosphorus. If there be much silicon, it occupies the place of the carbon, and then continued forging will not induce the carbon once separated to re-enter into combination. Such steel is easily burnt through and cannot be corrected; when burnt through, it is hard and cannot be annealed—this is tough steel, an inferior kind. Iron which contains sulphur and phosphorus cements badly, combines but little with carbon, and steel of this kind is brittle, both hot and cold. Iron in combination with the above-mentioned substances cannot be annealed by slow cooling, showing that these compounds are more stable than those of carbon and iron, and therefore they prevent the formation of the latter. Such metals as tin and zinc combine with iron, but not with carbon, and form a brittle mass which cannot be annealed and is deleterious to steel. Manganese and tungsten, on the contrary, are capable of combining with charcoal; they do not hinder the formation of steel, but even remove the injurious effects of other admixtures (by transforming these admixed substances into new compounds and slags), and are therefore ranked with the substances which act beneficially on steel; but, nevertheless, the best steel, which is capable of renewing most often its primitive qualities after burning or hot forging, is the purest. The addition of Ni, Cr, W, and certain other metals to steel renders it very suitable for certain special purposes, and is therefore frequently made use of.

It is worthy of attention that steel, besides temper, possesses many variable properties, a review of which may be made in the classification of the *sorts of steel* (1878, Cockerell). (1) *Very mild steel* contains from 0·05 to 0·20 p.c. of carbon, breaks with a weight of 40 to 50 kilos per square millimetre, and has an extension of 20 to 30 p.c.; it may be welded, like wrought iron, but cannot be tempered; is used in sheets for boilers, armour plate and bridges, nails, rivets, &c., as a substitute for wrought iron; (2) *mild steel*, from 0·20 to 0·35 p.c. of carbon, resistance to tension 50 to 60 kilos, extension 15 to 20 p.c., not easily welded, and tempers badly, used for axles, rails, and railway tyres, for cannons and guns, and for parts of machines destined to resist bending and torsion; (3 *hard steel*, carbon 0·35 to 0·50 p.c., breaking weight 60 to 70 kilos per square millimetre, extension 10 to 15 p.c., cannot be welded, takes a temper; used for rails, all kinds of springs, swords, parts of machinery in motion subjected to friction, hardness. Electro-deposited iron is brittle, but if heated (after the separation of the hydrogen) it becomes soft. If pure ferric hydroxide, which is easily prepared by the precipitation of solutions of ferric salts by means of ammonia, be heated in a stream of hydrogen, it forms, first of all, a dull black powder which ignites spontaneously in air (pyrophoric iron), and then a grey powder of pure iron. The powdery substance first obtained is an iron suboxide; when thrown into the air it ignites, forming the oxide Fe_3O_4. If the heating in hydrogen be continued, more water and pure iron, which does not ignite spontaneously, will be obtained. If a small quantity of iron be fused in the oxyhydrogen flame (with an excess of oxygen) in a piece of lime and mixed with powdered glass, pure molten iron will be formed, because in the oxyhydrogen flame iron melts and burns, but the substances mixed with the iron oxidise first. The oxidised impurities here either disappear (carbonic anhydride) in a gaseous form, or turn into slag (silica, manganese, oxide, and others)—that is, fuse with the glass. Pure iron has a silvery white colour and a specific gravity of 7·84; it melts at a temperature higher than the melting-points of silver, gold, nickel, and steel, *i.e.* about 1400°–1500° and

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spindles of looms, hammers, spades, hoes, &c.; (4) *very hard steel*, carbon 0·5 to 0·65 p.c., tensile breaking weight 70 to 80 kilos, extension 5 to 10 p.c., does not weld, but tempers easily; used for small springs, saws, files, knives and similar instruments.

The properties of ordinary *wrought iron* are well known. The best iron is the most tenacious—that is to say, that which does not break up when struck with the hammer or bent, and yet at the same time is sufficiently hard. There is, however, a distinction between hard and soft iron. Generally the softest iron is the most tenacious, and can best be welded, drawn into wire, sheets, &c. Hard, especially tough, iron is often characterised by its breaking when bent, and is therefore very difficult to work, and objects made from it are less serviceable in many respects. Soft iron is most adapted for making wire and sheet iron and such small objects as nails. Soft iron is characterised by its attaining a fibrous fracture after forging, whilst tough iron preserves its granular structure after this operation. Certain sorts of iron, although fairly soft at the ordinary temperature, become brittle when heated and are difficult to weld. These sorts are less suitable for being worked up into small objects. The variety of the properties of iron depends on the impurities which it contains. In general, the iron used in the arts still contains carbon and always a certain quantity of silicon, manganese, sulphur, phosphorus, &c. A variety in the proportion of these component parts changes the quality of the iron. In addition to this the change which soft wrought iron, having a fibrous structure, undergoes when subjected to repeated blows and vibrations is considerable; it then becomes granular and brittle. This to a certain degree explains the want of stability of some iron objects—such as truck axles, which must be renewed after a certain term of service, otherwise they become brittle. It is evident that there are innumerable intermediate transitions from wrought iron to steel and cast iron.

At the present day the greater part of the cast iron manufactured is converted into steel, generally cast steel (Bessemer's and Martin's). I may add the Urals, Donets district, and other parts of Russia offer the greatest advantages for the development of an iron industry, because these localities not only contain vast supplies of excellent iron ore, but also coal, which is necessary for smelting it.

below the melting point of platinum (1750°).[11] But pure iron becomes soft at a temperature considerably below that at which it melts, and may then be easily forged, welded, and rolled or drawn into sheets and wire.[11 bis] Pure iron may be rolled into an exceedingly thin sheet, weighing less than a sheet of ordinary paper of the same size. This ductility is the most important property of iron in all its forms, and is most marked with sheet iron, and least so with cast iron, whose ductility, compared with wrought iron, is small, but it is still very considerable when compared with other substances—such, for instance, as rocks.[12]

The chemical properties of iron have been already repeatedly mentioned in preceding chapters. Iron *rusts* in air at the ordinary temperature—that is to say, it becomes covered with a layer of iron oxides. Here, without doubt, the moisture of the air plays a part, because in dry air iron does not oxidise at all, and also because, more particularly, ammonia is always found in iron rust; the ammonia must arise from the action of the hydrogen of the water, at the moment of its separation, on the nitrogen of the air. Highly-polished steel does not rust nearly so readily, but if moistened with water, it easily becomes coated with rust. As rust depends on the access of moisture, iron may be preserved from rust by coating it with substances which prevent the moisture having access to it. Thus arises the practice of covering iron objects with paraffin,[13] varnish, oil, paints, or enamelling it with a glassy-looking flux possessing the same coefficient of expansion as iron, or with a dense scoria (formed by the heat of superheated steam), or with a compact coating of various metals. Wrought iron (both as sheet iron and in other forms), cast iron, and steel are often coated with tin, copper, lead, nickel, and similar metals, which prevent contact with the air. These metals preserve iron very effectually from rust if they form a completely compact surface, but in those places where the iron becomes exposed, either accidentally or from wear, rust appears much more quickly than on a uniform iron surface, because, towards these metals (and also towards the rust), the iron will then behave as an electro-positive pole in a galvanic couple, and hence will attract oxygen. A coating of zinc does not produce this inconvenience, because iron is electro-negative with reference to zinc, in consequence of which galvanised iron does not easily rust, and even an iron boiler containing some lumps of zinc rusts less than one without zinc.[14] Iron oxidises at a high temperature, forming *iron scale*, Fe_3O_4, composed of ferrous and ferric oxides, and, as has been seen, decomposes water and acids with the evolution of hydrogen. It is also capable of decomposing salts and oxides of other metals, which property is applied in the arts for the extraction of copper, silver, lead, tin, &c. For this reason iron is soluble in the solutions of many salts—for instance, in cupric sulphate, with precipitation of copper and formation of ferrous sulphate.[15] When iron *acts on acids* it always *forms compounds* FeX_2—

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[11] According to information supplied by A. T. Skinder's experiments at the Oboukoff Steel Works, 140 volumes of liquid molten steel give 128 volumes of solid metal. By means of a galvanic current of great intensity and dense charcoal as one electrode, and iron as the other, Bernadoss welded iron and fused holes through sheet iron. Soft wrought iron, like steel and soft malleable cast iron, may be melted in Siemens' regenerative furnaces, and in furnaces heated with naphtha.

[11 bis] Gore (1869), Tait, Barret, Tchernoff, Osmond, and others observed that at a temperature approaching 600°—that is, between dark and bright red heat—all kinds of wrought iron undergo a peculiar change called *recalescence*, *i.e.* a spontaneous rise of temperature. If iron be considerably heated and allowed to cool, it may be observed that at this temperature the cooling stops—that is, latent heat is disengaged, corresponding with a change in condition. The specific heat, electrical conductivity, magnetic, and other properties then also change. In tempering, the temperature of recalescence must not be reached, and so also in annealing, &c. It is evident that a change of the internal condition is here encountered, exactly similar to the transition from a solid to a liquid, although there is no evident physical change. It is probable that attentive study would lead to the discovery of a similar change in other substances.

[12] The particles of steel are linked together or connected more closely than those of the other metals; this is shown by the fact that it only breaks with a tensile strain of 60–80 kilos per sq. mm., whilst wrought iron only withstands about 30 kilos, cast iron 10, copper 35, silver 28, platinum 30, wood 8. The elasticity of iron, steel, and other metals is expressed by the so-called *coefficient of elasticity*. Let a rod be taken whose length is L; if a weight, P, be hung from the extremity of it, it will lengthen to *l*. The less it lengthens under other equal conditions, the more elastic the material, if it resumes its original length when the weight is removed. It has been shown by experiment that the increase in length *l*, due to elasticity, is directly proportional to the length L and the weight P, and inversely proportional to the section, but changes with the material. The coefficient of elasticity expresses that weight (in kilos per sq. mm.) under which a rod having a square section taken as 1 (we take 1 sq. mm.) acquires double the length by tension. Naturally in practice materials do not withstand such a lengthening, under a certain weight they attain a limit of elasticity, *i.e.* they stretch permanently (undergo deformation). Neglecting fractions (as the elasticity of metals varies not only with the temperature, but also with forging, purity, &c.), the coefficient of elasticity of steel and iron is 20,000, copper and brass 10,000, silver 7,000, glass 6,000, lead 2,000, and wood 1,200.

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[13] Paraffin is one of the best preservatives for iron against oxidation in the air. I found this by experiments about 1860, and immediately published the fact. This method is now very generally applied.

[14] See Chapter XVIII., Note 84 bis. Based on the rapid oxidation of iron and its increase in volume in the presence of water and salts of ammonium, a packing is used for water mains and steam pipes which is tightly hammered into the socket joints. This packing consists of a mixture of iron filings and a small quantity of sal-ammoniac (and sulphur) moistened with water; after a certain lapse of time, especially after the pipes have been used, this mass swells to such an extent that it hermetically seals the joints of the pipes.

[15] Here, however, a ferric salt may also be formed (when all the iron has dissolved and the cupric salt is still in excess), because the cupric salts are reduced by ferrous salts. Cast iron is also dissolved.

that is, corresponding to the suboxide FeO – and answering to magnesium compounds—and hence two atoms of hydrogen are replaced by one atom of iron. Strongly oxidising acids like nitric acid may transform the ferrous salt which is forming into the higher degree of oxidation or ferric salt (corresponding with the sesquioxide, Fe_2O_3), but this is a secondary reaction. Iron, although easily soluble in dilute nitric acid, loses this property when plunged into strong fuming nitric acid; after this operation it even loses the property of solubility in other acids until the external coating formed by the action of the strong nitric acid is mechanically removed. This condition of iron is termed the passive state. *The passive condition* of iron depends on the formation, on its surface, of a coating of oxide due to the iron being acted on by the lower oxides of nitrogen contained in the fuming nitric acid.[16] Strong nitric acid which does not contain these lower oxides, does not render iron passive, but it is only necessary to add some alcohol or other reducing agent which forms these lower oxides in the nitric acid, and the iron will assume the passive state.

Iron readily combines with non-metals—for instance, with chlorine, iodine, bromine, sulphur, and even with phosphorus and carbon; but on the other hand the property of combining with metals is but little developed in it—that is to say, it does not easily form alloys. Mercury, which acts on most metals, does not act directly on iron, and the *iron amalgam*, or solution of iron in mercury, which is used for electrical machines, is only obtained in a particular way—namely, with the co-operation of a sodium amalgam, in which the iron dissolves and by means of which it is reduced from solutions of its salts.

When iron acts on acids it forms ferrous salts of the type FeX_2, and in the presence of air and oxidising agents they change by degrees into ferric salts of the type FeX_3. This faculty of passing from the ferrous to the ferric state is still further developed in ferrous hydroxide. If sodium hydroxide be added to a solution of ferrous sulphate or green vitriol, $FeSO_4$,[17] a white precipitate of ferrous hydroxide, FeH_2O_2,

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[16] Powdery reduced iron is passive with regard to nitric acid of a specific gravity of 1·37, but when heated the acid acts on it. This passiveness disappears in the magnetic field. Saint-Edme attributes the passiveness of iron (and nickel) to the formation of nitride of iron on the surface of the metal, because he observed that when heated in dry hydrogen ammonia is evolved by passive iron.

Remsen observed that if a strip of iron be immersed in acid and placed in the magnetic field, it is principally dissolved at the middle part—that is, the acid acts more feebly at the poles. According to Étard (1891) strong nitric acid dissolves iron in making it passive, although the action is a very slow one.

[17] *Iron vitriol or green vitriol*, sulphate of iron or ferrous sulphate, generally crystallises from solutions, like magnesium sulphate, with seven molecules of water, $FeSO_4,7H_2O$. This salt is not only formed by the action of iron on sulphuric acid, but

$= Fe_2Cl_6$, or, generally speaking, $2FeO + Cl_2 + H_2O = Fe_2O_3 + 2HCl$ When such a transformation is required it is best to add potassium chlorate and hydrochloric acid to the ferrous solution; chlorine is formed by their mutual reaction and acts as an oxidising agent. Nitric acid produces a similar effect, although more slowly Ferrous salts may be completely and rapidly oxidised into ferric salts by means of chromic acid or permanganic acid, $HMnO_4$, in the presence of acids—for example, $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$. This reaction is easily observed by the change of colour, and its termination is easily seen, because potassium permanganate forms solutions of a bright red colour, and when added to a solution of a ferrous salt the above reaction immediately takes place *in the presence of acid*, and the solution then becomes colourless, because all the substances formed are only faintly coloured in solution. Directly all the ferrous compound has passed into the ferric state, any excess of permanganate which is added communicates a red colour to the liquid (see Chapter XXI.)

Thus when ferrous salts are acted on by oxidising agents, they pass into the ferric form, and under the action of reducing agents the reverse reaction occurs. Sulphuretted hydrogen may, for instance, be used for this complete transformation, for under its influence ferric salts are reduced with separation of sulphur—for example, $Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S$. Sodium thiosulphate acts in a similar way: $Fe_2Cl_6 + Na_2S_2O_3 + H_2O = 2FeCl_2 + Na_2SO_4 + 2HCl + S$. Metallic iron or zinc,[20] in the presence of acids, or sodium amalgam, &c., acts like hydrogen, and has also a similar reducing action, and this furnishes the best method for reducing ferric salts to ferrous salts—for instance, $Fe_2Cl_6 + Zn = 2FeCl_2 + ZnCl_2$. Thus *the transition from ferrous salts to ferric salts and vice versâ is always possible.*[21]

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[20] Copper and cuprous salts also reduce ferric oxide to ferrous oxide, and are themselves turned into cupric salts. The essence of the reactions is expressed by the following equations. $Fe_2O_3 + Cu_2O + 2FeO + 2CuO$; $Fe_2O_3 + Cu = 2FeO + CuO$. This fact is made use of in analysing copper compounds, the quantity of copper being ascertained by the amount of ferrous salt obtained. An excess of ferric salt is required to complete the reaction. Here we have an example of reverse reaction; the ferrous oxide or its salt in the presence of alkali transforms the cupric oxide into cuprous oxide and metallic copper, as observed by Lovel, Knopp, and others.

[21] We will here mention the reactions by means of which it may be ascertained whether the ferrous compound has been entirely converted into a ferric compound or *vice versâ*. There are two substances which are best employed for this purpose: potassium ferricyanide, $FeK_3C_6N_6$, and potassium thiocyanate, KCNS. The first salt gives with ferrous salts a blue precipitate of an insoluble salt, having a composition $Fe_5C_{12}N_{12}$; but with ferric salts it does not form any precipitate, and only gives a brown colour, and therefore when transforming a ferrous salt into a ferric salt, the completion of the transformation may be detected by taking a drop of the liquid on paper or on a porcelain plate and adding a drop of the ferricyanide solution. If a blue precipitate be

Ferric oxide, or *sesquioxide of iron*, Fe_2O_3, is found in nature, and is artificially prepared in the form of a red powder by many methods. Thus after heating green vitriol a red oxide of iron remains, called colcothar, which is used as an oil paint, principally for painting wood. The same substance in the form of a very fine powder (rouge) is used for polishing glass, steel, and other objects. If a mixture of ferrous sulphate with an excess of common salt be strongly heated, crystalline ferric oxide will be formed, having a dark violet colour, and resembling some natural varieties of this substance. When iron pyrites is heated for preparing sulphurous anhydride, ferric oxide also remains behind; it is used as a pigment. On the addition of alkalis to a solution of ferric salts, a brown precipitate of ferric hydroxide is formed, which when heated (even when boiled in water, that is, at about 100°, according to Tomassi) easily parts with the water, and leaves red anhydrous ferric oxide. Pure ferric oxide does not show any magnetic properties, but when heated to a white heat it loses oxygen and is converted into the magnetic oxide. Anhydrous ferric oxide which has been heated to a high temperature is with difficulty soluble in acids (but it is soluble when heated in strong acids, and also when fused with potassium hydrogen sulphate), whilst ferric hydroxide, at all events that which is precipitated from salts by means of alkalis, is very readily soluble in acids. The precipitated *ferric hydroxide* has the composition $2Fe_2O_3,3H_2O$, or $Fe_4H_6O_9$. If this ordinary hydroxide be rendered anhydrous (at 100°), at a certain moment it becomes incandescent —that is, loses a certain quantity of heat. This self incandescence depends on internal displacement produced by the transition of the easily soluble (in acids) variety into the difficultly-soluble variety, and does not depend on the loss of water, since the anhydrous oxide undergoes the same change. In addition to this there exists a ferric hydroxide, or hydrated oxide of iron, which, like the strongly-heated anhydrous iron oxide, is difficultly soluble in acids. This hydroxide on losing water, or after the loss of water, does not undergo such self-incandescence, because no such state of internal displacement occurs (loss of energy or heat) with it as that which is peculiar to the ordinary oxide of iron. The ferric hydroxide which is difficultly soluble in acids has the composition Fe_2O_3,H_2O. This hydroxide is obtained by a pro-

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formed, then part of the ferrous salt still remains; if there is none, the transformation is complete. The thiocyanate does not give any marked colouration with ferrous salts; but with ferric salts in the most diluted state it forms a bright red soluble compound, and therefore when transforming a ferric salt into a ferrous salt we must proceed as before, testing a drop of the solution with thiocyanate, when the absence of a red colour will prove the total transformation of the ferric salt into the ferrous state, and if a red colour is apparent it shows that the transformation is not yet complete.

longed ebullition of water in which ferric hydroxide prepared by the oxidation of ferrous oxide is suspended, and also sometimes by similar treatment of the ordinary hydroxide after it has been for a long time in contact with water. The transition of one hydroxide to another is apparent by a change of colour; the easily-soluble hydroxide is redder, and the sparingly-soluble hydroxide more yellow in colour.[22]

The normal salts of the composition Fe_2X_6 or FeX_3 correspond with ferric oxide—for example, the exceedingly volatile *ferric chloride*, Fe_2Cl_6, which is easily prepared in the anhydrous state by the action of chlorine on heated iron.[23] Such also is the *normal ferric nitrate*,

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[22] The two ferric hydroxides are not only characterised by the above-mentioned properties, but also by the fact that the first hydroxide forms immediately with potassium ferrocyanide, $K_4FeC_6N_6$, a blue colour depending on the formation of Prussian blue, whilst the second hydroxide does not give any reaction whatever with this salt. The first hydroxide is entirely soluble in nitric, hydrochloric, and all other acids; whilst the second sometimes (not always) forms a brick-coloured liquid, which appears turbid and does not give the reactions peculiar to the ferric salts (Péan de Saint-Gilles, Scheurer-Kestner). In addition to this, when the smallest quantity of an alkaline salt is added to this liquid, ferric oxide is precipitated. Thus a colloidal solution is formed (hydrosol), which is exactly similar to silica hydrosol (Chapter XVII.), according to which example the hydrosol of ferric oxide may be obtained.

If ordinary ferric hydroxide be dissolved in acetic acid, a solution of the colour of red wine is obtained, which has all the reactions characteristic of ferric salts. But if this solution (formed in the cold) be heated to the boiling-point, its colour is very rapidly intensified, a smell of acetic acid becomes apparent, and the solution then contains a new variety of ferric oxide. If the boiling of the solution be continued, acetic acid is evolved, and the modified ferric oxide is precipitated. If the evaporation of the acetic acid be prevented (in a closed or sealed vessel), and the liquid be heated for some time, the whole of the ferric hydroxide then passes into the insoluble form, and if some alkaline salt be added (to the hydrosol formed), the whole of the ferric oxide is then precipitated in its insoluble form. This method may be applied for separating ferric oxide from solutions of its salts.

All phenomena observed respecting ferric oxide (colloidal properties, various forms, formation of double basic salts) demonstrate that this substance, like silica, alumina, lead hydroxide, &c., is polymerised, that the composition is represented by $(Fe_2O_3)_n$.

[23] The ferric compound which is most used in practice (for instance, in medicine, for cauterising, stopping bleeding, &c.—Oleum Martis) is *ferric chloride*, Fe_2Cl_6, easily obtained by dissolving the ordinary hydrated oxide of iron in hydrochloric acid. It is obtained in the anhydrous state by the action of chlorine on heated iron. The experiment is carried on in a porcelain tube, and a solid *volatile substance* is then formed in the shape of brilliant violet scales which very readily absorb moisture from the air, and when heated with water decompose into crystalline ferric oxide and hydrochloric acid: $Fe_2Cl_6 + 3H_2O = 6HCl + Fe_2O_3$. Ferric chloride is so volatile that the density of its vapour may be determined. At 440° it is equal to 164·0 referred to hydrogen; the formula Fe_2Cl_6 corresponds with a density of 162·5. An aqueous solution of this salt has a brown colour. On evaporating and cooling this solution, crystals separate containing 6 or 12 molecules of H_2O. Ferric chloride is not only soluble in water, but also in alcohol (similarly to magnesium chloride, &c.) and in ether. If the latter solutions are exposed to the rays of the sun they become colourless, and deposit ferrous chloride, $FeCl_2$, chlorine being disengaged. After a certain lapse of time, the aqueous solutions of ferric chloride decompose with precipitation of a basic salt, thus demonstrating the instability of ferric chloride, like the other salts of ferric oxide (Note 22). This salt is

$Fe_2(NO_3)_6$; it is obtained by dissolving iron in an excess of nitric acid,

much more stable in the form of double salts, like all the ferric salts and also the salts of many other feeble bases. Potassium or ammonium chloride forms with it very beautiful red crystals of a double salt, having the composition $Fe_2Cl_6,4KCl,2H_2O$. When a solution of this salt is evaporated it decomposes, with separation of potassium chloride.

B. Roozeboom (1892) studied in detail (as for $CaCl_2$, Chapter XIV., Note 50) the separation of different hydrates from saturated solutions of Fe_2Cl_6 at various concentrations and temperatures; he found that there are 4 crystallohydrates with 12, 7, 5, and 4 molecules of water. An orange yellow only slightly hygroscopic hydrate, $Fe_2Cl_6,12H_2O$, is most easily and usually obtained, which melts at 37°; its solubility at different temperatures is represented by the curve BCD in the accompanying figure, where the point B

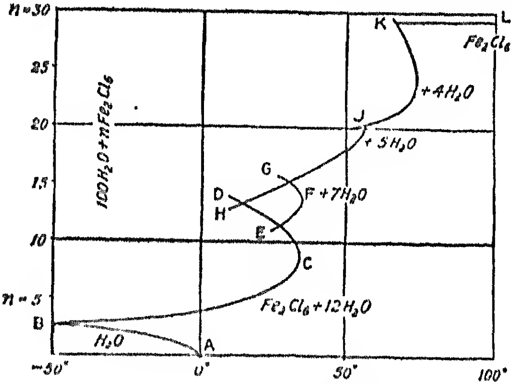

FIG. 95.—Diagram of the solubility of Fe_2Cl_6

corresponds to the formation, at −55°, of a cryohydrate containing about $Fe_2Cl_6 + 36H_2O$, the point C corresponds to the melting-point (+37°) of the hydrate $Fe_2Cl_6,12H_2O$, and the curve CD to the fall in the temperature of crystallisation with an increase in the amount of salt, or decrease in the amount of water (in the figure the temperatures are taken along the axis of abscissæ, and the amount of *n* in the formula $nFe_2Cl_6 + 100H_2O$ along the axis of ordinates). When anhydrous Fe_2Cl_6 is added to the above hydrate ($12H_2O$), or some of the water is evaporated from the latter, very hygroscopic crystals of $Fe_2Cl_6,5H_2O$ (Fritsche) are formed; they melt at 56°, their solubility is expressed by the curve HJ, which also presents a small branch at the end J. This again gives the fall in the temperature of crystallisation with an increase in the amount of Fe_2Cl_6. Besides these curves and the solubility of the anhydrous salt expressed by the line KL (up to 100°, beyond which chlorine is liberated), Roozeboom also gives the two curves, EFG and JK, corresponding to the crystallohydrates, $Fe_2Cl_6,7H_2O$ (melts at +32°·5, that is lower than any of the others) and $Fe_2Cl_6,4H_2O$ (melts at 73°·5), which he discovered by a systematic research on the solutions of ferric chloride. The curve AB represents the separation of ice from dilute solutions of the salt.

The researches of the same Dutch chemist upon the conditions of the formation of crystals from the double salt $(NH_4Cl)_4Fe_2Cl_6,2H_2O$ are even more perfect. This salt was obtained in 1839 by Fritsche, and is easily formed from a strong solution of Fe_2Cl_6 by adding sal-ammoniac, when it separates in crimson rhombic crystals, which, after dissolving in water, only deposit again on evaporation, together with the sal-ammoniac.

Roozeboom (1892) found that when the solution contains *b* molecules of Fe_2Cl_6, and taking care as far as possible to prevent any rise of temperature.[24] The normal salt separates from the brown solution when it is concentrated

a molecules of NH_4Cl, per 100 molecules H_2O, then at 15° one of the following separations takes place: (1) crystals, $Fe_2Cl_6,12H_2O$, when *a* varies between 0 and 11, and *b* between 4·65 and 4·8, or (2) a mixture of these crystals and the double salt, when *a* = 1·86, and *b* = 4·47, or (3) the double salt, $Fe_2Cl_6,4NH_4Cl,2H_2O$, when *a* varies between 2 and 11·8, and *b* between 3·1 and 4·56, or (4) a mixture of sal-ammoniac with the iron salt (it crystallises in separate cubes, Retgers, Lehmann), when *a* varies between 7·7 and 10·9, and *b* is less than 3·88, or (5) sal-ammoniac, when *a* = 11·88. And as in the double salt, *a* : *b* :: 4 : 1 it is evident that the double salt only separates out when the ratio *a* : *b* is less than 4 . 1 (*i.e.* when Fe_2Cl_6 predominates). The above is seen more clearly in the accompanying figure, where *a*, or the number of molecules of NH_4Cl per $100H_2O$, is taken along the axis of abscissæ, and *b*, or the number of molecules of Fe_2Cl_6, along the ordinates. The curves ABCD correspond to saturation and present an iso-therm of 15°. The portion AB corresponds to the separation of chloride of iron (the ascending nature of this curve shows that the solubility of Fe_2Cl_6 is increased by the presence of NH_4Cl, while that of NH_4Cl decreases in the presence of Fe_2Cl_6), the portion BC to the double salt, and the portion CD to a mixture of sal-ammoniac and ferric chloride, while the straight line OF corresponds to the ratio $Fe_2Cl_6,4NH_4Cl$, or *a* : *b* :: 4 : 1. The portion CE shows that more double salt may be introduced into the solution without decomposition, but then the solution deposits a mixture of sal-ammoniac and ferric chloride (*see* Chapter XXIV. Note 9 bis). If there were more such well-investigated cases of solutions, our knowledge of double salts, solutions, the influence of water, equilibria, isomorphous mixtures, and such-like provinces of chemical relations might be considerably advanced.

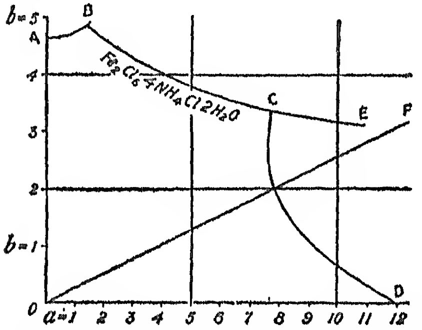

Fig. 96.—Diagram of the formation, at 15°, of the double salt $Fe_2Cl_6 4NH_4Cl 2H_2O$ or $Fe(NH_4)_2Cl_5,H_2O$. (After Roozeboom.)

[24] The normal ferric salts are decomposed by heat and even by water, forming basic salts, which may be prepared in various ways. Generally ferric hydroxide is dissolved in solutions of ferric nitrate; if it contains a double quantity of iron the basic salt is formed which contains Fe_2O_3 (in the form of hydroxide) $+ 2Fe_2(NO_3)_6 = 3Fe_2O(NO_3)_4$, a salt of the type Fe_2OX_4. Probably water enters into its composition. With considerable quantities of ferric oxide, insoluble basic salts are obtained containing various amounts of ferric hydroxide. Thus when a solution of the above-mentioned basic acid is boiled, a precipitate is formed containing $4(Fe_2O_3)_3,2(N_2O_5),3H_2O$, which probably contains $2Fe_2O_2(NO_3)_2 + 2Fe_2O_3,3H_2O$ If a solution of basic nitrate be sealed in a tube and then immersed in boiling water, the colour of the solution changes just in the same way as if a solution of ferric acetate had been employed (Note 22). The solution obtained smells strongly of nitric acid, and on adding a drop of sulphuric or hydrochloric acid the insoluble variety of hydrated ferric oxide is precipitated.

Normal ferric *orthophosphat* is soluble in sulphuric, hydrochloric, and nitric acids, but insoluble in others, such as, for instance, acetic acid. The composition of this salt in the anhydrous state is $FePO_4$, because in orthophosphoric acid there are three atoms of hydrogen, and iron, in the ferric state, replaces the three atoms of hydrogen. This salt is obtained from ferric acetate, which, with disodium phosphate, forms a *white pre-*

under a bell jar over sulphuric acid. This salt, $Fe_2(NO_3)_6,9H_2O$, then crystallises in well-formed and perfectly colourless crystals,[25] which deliquesce in air, melt at 35°, and are soluble in and decomposed by water. The decomposition may be seen from the fact that the solution is brown and does not yield the whole of the salt again, but gives partly basic salt. The normal salt (only stable in the presence of an excess of HNO_3) is completely decomposed with great facility by heating with water, even at 130°, and this is made use of for removing iron (and also certain other oxides of the form R_2O_3) from many other bases (of the form RO) whose nitrates are far more stable. The ferric salts, FeX_3, in passing into ferrous salts, act as oxidising agents, as is seen from the fact that they not only liberate S from SH_2, but also iodine from KI like many oxidising agents.[25 bis]

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cipitate of $FePO_4$, containing water. If a solution of ferric chloride (yellowish-red colour) be mixed with a solution of sodium acetate in excess, the liquid assumes an intense brown colour which demonstrates the formation of a certain quantity of ferric acetate; then the disodium phosphate directly forms a white gelatinous precipitate of ferric phosphate. By this means the whole of the iron may be precipitated, and the liquid which was brown then becomes colourless. If this normal salt be dissolved in orthophosphoric acid, the crystalline acid salt $FeH_3(PO_4)_2$ is formed. If there be an excess of ferric oxide in the solution, the precipitate will consist of the basic salt. If ferric phosphate be dissolved in hydrochloric acid, and ammonia be added, a salt is precipitated on heating which, after continued washing in water and heating (to remove the water), has the composition $Fe_4P_2O_{11}$—that is, $2Fe_2O_3,P_2O_5$. In an aqueous condition this salt may be considered as ferric hydroxide, $Fe_2(OH)_6$, in which $(OH)_3$ is replaced by the equivalent group PO_4. Whenever ammonia is added to a solution containing an excess of ferric salt and a certain amount of phosphoric acid, a precipitate is formed containing the whole of the phosphoric acid in the mass of the ferric oxide.

Ferric oxide is characterised as a feeble base, and also by the fact of its forming double salts—for instance, *potassium iron alum*, which has a composition $Fe_2(SO_4)_3,K_2SO_4,24H_2O$ or $FeK(SO_4)_2,12H_2O$. It is obtained in the form of almost colourless or light rose-coloured large octahedra of the regular system by simply mixing solutions of potassium sulphate and the ferric sulphate obtained by dissolving ferric oxide in sulphuric acid.

[25] It would seem that all normal ferric salts are colourless, and that the brown colour which is peculiar to the solutions is really due to basic ferric salts. A remarkable example of the apparent change of colour of salts is represented by the ferrous and ferric oxalates. The former in a dry state has a yellow colour, although as a rule the ferrous salts are green, and the latter is colourless or pale green. When the normal ferric salt is dissolved in water it is, like many salts, probably decomposed by the water into acid and basic salts, and the latter communicates a brown colour to the solution. Iron alum is almost colourless, is easily decomposed by water, and is the best proof of our assertion. The study of the phenomena peculiar to ferric nitrate might, in my opinion, give a very useful addition to our knowledge of the aqueous solutions of salts in general.

[25 bis] The reaction $FeX_3 + KI = FeX_2 + KX + I$ proceeds comparatively slowly in solutions, is not complete (depends upon the mass), and is reversible. In this connection we may cite the following data from Seubert and Rohrer's (1894) comprehensive researches. The investigations were conducted with solutions containing $\frac{1}{10}$ gram—equivalent weights of $Fe_2(SO_4)_3$ (*i.e.* containing 20 grams of salt per litre), and a corresponding solution of KI; the amount of iodine liberated being determined (after the addition of starch) by a solution (also $\frac{1}{10}$ normal) of $Na_2S_2O_3$ (*see* Chapter XX., Note 42). The pro-

Iron forms one other oxide besides the ferric and ferrous oxides; this contains twice as much oxygen as the former, but is so very unstable that it can neither be obtained in the free state nor as a hydrate. Whenever such conditions of double decomposition occur as should allow of its separation in the free state, it decomposes into oxygen and ferric oxide. It is known in the state of salts, and is only stable in the presence of alkalis, and forms salts with them which have a decidedly alkaline reaction; it is therefore a feebly acid oxide. Thus when small pieces of iron are heated with nitre or potassium chlorate a potassium salt of the composition K_2FeO_4 is formed, and therefore the hydrate corresponding with this salt should have the composition H_2FeO_4. It is called *ferric acid.* Its anhydride ought to contain FeO_3 or Fe_2O_6—twice as much oxygen as ferric oxide. If a solution of potassium ferrate be mixed with acid, the free hydrate ought to be formed, but it immediately decomposes ($2K_2FeO_4 + 5H_2SO_4 = 2K_2SO_4 + Fe_2(SO_4)_3 + 5H_2O + O_3$), oxygen being evolved. If a small quantity of acid be taken, or if a solution of potassium ferrate be heated with solutions of other metallic salts, ferric oxide is separated—for instance:

$$2CuSO_4 + 2K_2FeO_4 = 2K_2SO_4 + O_3 + Fe_2O_3 + 2CuO.$$

Both these oxides are of course deposited in the form of hydrates. This shows that not only the hydrate H_2FeO_4, but also the salts of the heavy metals corresponding with this higher oxide of iron, are not formed by reactions of double decomposition. The solution of potassium ferrate naturally acts as a powerful oxidising agent; for instance, it transforms manganous oxide into the dioxide, sulphurous into sulphuric acid, oxalic acid into carbonic anhydride and water, &c.[26]

Iron thus combines with oxygen in three proportions: RO, R_2O_3,

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gress of the reaction was expressed by the amount of liberated iodine in percentages of the theoretical amount. For instance, the following amount of iodide of potassium was decomposed when $Fe_2(SO_4)_3 + 2nKI$ was taken:

n =	1	2	3	6	10	20
After 15′	11·4	26·3	40·6	73·5	91·6	96·0
„ 30′	14·0	35·8	47·8	78·5	94·8	97·4
„ 1 hour	19·0	42·7	56·0	84·0	95·7	97·6
„ 10 „	32·6	56·0	75·7	93·2	96·5	97·6
„ 48 „	39·4	67·7	82·6	98·4	96·6	97·6

Similar results were obtained for $FeCl_3$, but then the amount of iodine liberated was somewhat greater. Similar results were also obtained by increasing the mass of FeX_3 per KI, and by replacing it by HI (*see* Chapter XXI., Note 26).

[26] If chlorine be passed through a strong solution of potassium hydroxide in which hydrated ferric oxide is suspended, the turbid liquid acquires a dark pomegranate-red colour and contains potassium ferrate: $10KHO + Fe_2O_3 + 3Cl_2 = 2K_2FeO_4 + 6KCl + 5H_2O$. The chlorine must not be in excess, otherwise the salt is again decomposed, although the mode of decomposition is unknown; however, ferric chloride and potassium chlorate are probably formed. Another way in which the above-described salt is formed is also

and RO_3. It might have been expected that there would be intermediate stages RO_2 (corresponding to pyrites FeS_2) and R_2O_5, but for iron these are unknown.[26 bis] The lower oxide has a distinctly basic character, the higher is feebly acid. The only one which is stable in the free state is ferric oxide, Fe_2O_3; the suboxide, FeO, absorbs oxygen, and ferric anhydride, FeO_3, evolves it. It is also the same for other elements; the character of each is determined by the relative degree of stability of the known oxides. The salts FeX_2 correspond with the suboxide, the salts FeX_3 or Fe_2X_6 with the sesquioxide, and FeX_6 represents those of ferric acid, as its potassium salt is $FeO_2(OK)_2$, corresponding with K_2SO_4, K_2MnO_4, K_2CrO_4, &c. Iron therefore forms compounds of the types FeX_2, FeX_3, and FeX_6, but this latter, like the type NX_5, does not appear separately, but only when X represents heterogeneous elements or groups; for instance, for nitrogen in the form of $NO_2(OH)$, NH_4Cl, &c., for iron in the form of $FeO_2(OK)_2$. But still the type FeX_6 exists, and therefore FeX_2 and FeX_3 are compounds which, like ammonia, NH_3, are capable of further combinations up to FeX_6; this is also seen in the property of ferrous and ferric salts of forming compounds with water of crystallisation, besides double and basic salts, whose stability is determined by the quality of the elements included in the types FeX_2 and FeX_3.[26 tri] It is therefore to be expected that there should be complex compounds

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remarkable; a galvanic current (from 6 Grove elements) is passed through cast iron and platinum electrodes into a strong solution of potassium hydroxide. The cast-iron electrode is connected with the positive pole, and the platinum electrode is surrounded by a porous earthenware cylinder. Oxygen would be evolved at the cast-iron electrode, but it is used up in oxidation, and a dark solution of potassium ferrate is therefore formed about it. It is remarkable that the cast iron cannot be replaced by wrought iron.

[26 bis] When Mond and his assistants obtained the remarkable volatile compound $Ni(CO)_4$ (described later, Chapter XXII.), it was shown subsequently by Mond and Quincke (1891), and also by Berthelot, that iron, under certain conditions, in a stream of carbonic oxide, also volatilises and forms a compound like that given by nickel. Roscoe and Scudder then showed that when water gas is passed through and kept under pressure (8 atmospheres) in iron vessels a portion of the iron volatilises from the sides of the vessel, and that when the gas is burnt it deposits a certain amount of oxides of iron (the same result is obtained with ordinary coal gas which contains a small amount of CO). To obtain the *volatile compound of iron with carbonic oxide*, Mond prepared a finely divided iron by heating the oxalate in a stream of hydrogen, and after cooling it to 80°—45° he passed CO over the powder. The iron then formed (although very slowly) a volatile compound containing $Fe(CO)_5$ (as though it answered to a very high type, FeX_{10}), which when cooled condenses into a liquid (slightly coloured, probably owing to incipient decomposition), sp. gr. 1·47, which solidifies at −21°, boils at about 103°, and has a vapour density (about 6·5 with respect to air) corresponding to the above formula; it decomposes at 180°. Water and dilute acids do not act upon it, but it decomposes under the action of light and forms a hard, non-volatile crystalline yellow compound $Fe_2(CO)_7$ which decomposes at 80° and again forms $Fe(CO)_5$.

[26 tri] When the molecular Fe_2Cl_6 is produced instead of $FeCl_3$ this complication of the type also occurs.

derived from ferrous and ferric oxides. Amongst these the series of cyanogen compounds is particularly interesting; their formation and character is not only determined by the property which iron possesses of forming complex types, but also by the similar faculty of the cyanogen compounds, which, like nitriles (Chapter IX.), have clearly developed properties of polymerisation and in general of forming complex compounds.[27]

In the cyanogen compounds of iron, two degrees might be expected: $Fe(CN)_2$, corresponding with ferrous oxide, and $Fe(CN)_3$, corresponding with ferric oxide. There are actually, however, many other known compounds, intermediate and far more complex. They correspond with the double salts so easily formed by metallic cyanides. The two following double salts are particularly well known, very stable, often used, and easily prepared. *Potassium ferrocyanide* or *yellow prussiate of potash*, a double salt of cyanide of potassium and ferrous cyanide, has the composition $FeC_2N_2,4KCN$; its crystals contain 3 mol. of water: $K_4FeC_6N_6,3H_2O$. The other is *potassium ferricyanide* or *red prussiate of potash*. It is also known as *Gmelin's salt*, and contains cyanide of potassium with ferric cyanide; its composition is $Fe(CN)_3,3KCN$ or $K_3FeC_6N_6$. Its crystals do not contain water. It is obtained from the first by the action of chlorine, which removes one atom of the potassium. A whole series of other ferrocyanic compounds correspond with these ordinary salts.

Before treating of the preparation and properties of these two remarkable and very stable salts, it must be observed that with ordinary reagents neither of them gives the same double decompositions as the other ferrous and ferric salts, and they both present a series of remarkable properties. Thus these salts have a neutral reaction, are unchanged by air, dilute acids, or water, unlike potassium cyanide and even some of its double salts. When solutions of these salts are treated with caustic alkalis, they do not give a precipitate of ferrous or ferric hydroxides, neither are they precipitated by sodium carbonate. This led the earlier investigators to recognise special independent groupings in them. The yellow prussiate was considered to contain the complex radicle FeC_6N_6 combined with potassium, namely with K_4, and K_3 was attributed to the red prussiate. This was confirmed by the fact that whilst in both salts any other metal, even hydrogen, might be substituted for potassium, the iron remained unchangeable, just as nitrogen in cyanogen, ammonium, and nitrates does not enter into double decomposition, being in the state of the complex radicles CN, NH_4, NO_2. Such a representation is, however, completely superfluous for the explanation of the peculiarities in the reactions of such compounds as double salts. If a magnesium salt which can be precipitated by potassium hydroxide does not form a precipitate in the presence of ammonium chloride, it is very clear that it is owing to the formation of a soluble double salt which is not decomposed by alkalis. And there is no necessity to account for the peculiarity of reaction of a double salt by the formation of a new complex radicle. In the same way also, in the presence of an excess of tartaric acid, cupric salts do not form a precipitate with potassium hydroxide, because a double salt is formed. These peculiarities are more easily understood in the case of cyanogen compounds than in all others, because all cyanogen compounds, as unsaturated compounds, show a marked tendency to complexity. This tendency is satisfied in double salts. The appearance of a peculiar character in double cyanides is the more easily understood since in the case of potassium cyanide itself, and also in hydrocyanic acid, a great many peculiarities have been observed which are not encountered in those haloid compounds, potassium chloride and hydrochloric acid, with which it was usual to compare cyanogen compounds. These peculiarities become more comprehensible on comparing cyanogen compounds with ammonium compounds. Thus in the presence of ammonia the reactions of many compounds change considerably. If in addition to this it is remembered that the presence of many carbon (organic) compounds frequently completely disturbs the reaction of salts, the peculiarities of certain double cyanides will appear still less strange, because they contain carbon. The fact that the presence of carbon or another element in the compound produces a change in the reactions, may be compared to the action of oxygen, which, when entering into a combination, also very materially changes the nature of reactions. Chlorine is not detected by silver nitrate when it is in the form of potassium chlorate, $KClO_3$, as it is detected in potassium chloride, KCl. The iron in ferrous and ferric compounds varies in its reactions. In addition to the above-mentioned facts, consideration ought to be given to the circumstance that the easy mutability of nitric acid undergoes modification in its alkali salts, and in general the properties of a salt often differ much from those of the acid. Every double salt ought to be regarded as a peculiar kind of saline compound: potassium cyanide is, as it were, a basic, and ferrous cyanide an acid, element. They may be unstable in the separate state, but form a stable double compound when combined together; the act of combination disengages the energy of the elements, and they, so to speak, saturate each other. Of course, all this is not a definite explanation, but then the supposition of a special complex radicle can even less be regarded as such.

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[27] Some light may be thrown upon the faculty of Fe of forming various compounds with CN, by the fact that Fe not only combines with carbon but also with nitrogen. *Nitride of iron* Fe_2N was obtained by Fowler by heating finely powdered iron in a stream of NH_3 at the temperature of melting lead.

Potassium ferrocyanide, $K_4FeC_6N_6$, is very easily formed by mixing solutions of ferrous sulphate and potassium cyanide. First, a white precipitate of ferrous cyanide, FeC_2N_2, is formed, which becomes blue on exposure to air, but is soluble in an excess of potassium cyanide, forming the ferrocyanide. The same yellow prussiate is obtained on heating animal nitrogenous charcoal or animal matters—such as horn, leather cuttings, &c.—with potassium carbonate in iron vessels,[27 bis] the mass formed being afterwards boiled with water with exposure to air, potassium cyanide first appearing, which gives yellow prussiate. The animal charcoal may be exchanged for wood charcoal, permeated with potassium carbonate and heated in nitrogen or ammonia; the mass thus produced is then boiled in water with ferric oxide.[28] In this manner it is manufactured on the large scale, and is called 'yellow prussiate' ('prussiate de potasse,' Blutlaugensalz).

It is easy to substitute other metals for the potassium in the yellow prussiate. The hydrogen salt or hydroferrocyanic acid, $H_4FeC_6N_6$, is obtained by mixing strong solutions of yellow prussiate and hydrochloric acid. If ether be added and the air excluded, the acid is obtained directly in the form of a white scarcely crystalline precipitate which becomes blue on exposure to air (as ferrous cyanide does from the formation of blue compounds of ferrous and ferric cyanides, and it is on this account used in cotton printing). It is soluble in water and alcohol, but not in ether, has marked acid properties, and decomposes carbonates, which renders it easily possible to prepare ferrocyanides of

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[27 bis] The sulphur of the animal refuse here forms the compound $FeKS_2$, which by the action of potassium cyanide yields potassium sulphide, thiocyanate, and ferrocyanide.

[28] Potassium ferrocyanide may also be obtained from Prussian blue by boiling with a solution of potassium hydroxide, and from the ferricyanide by the action of alkalis and reducing substances (because the red prussiate is a product of oxidation produced by the action of chlorine: a ferric salt is reduced to a ferrous salt), &c. In many works (especially in Germany and France) yellow prussiate is prepared from the mass, containing oxide of iron, and employed for purifying coal gas (Vol. I., p. 361), which generally contains cyanogen compounds. About 2 p.c. of the nitrogen contained in coal is converted into cyanogen, which forms Prussian blue and thiocyanates in the mass used for purifying the gas. On evaporation the solution yields large yellow crystals containing 3 molecules of water, which is easily expelled by heating above 100°. 100 parts of water at the ordinary temperature are capable of dissolving 25 parts of this salt; its sp. gr. is 1·83. When ignited it forms potassium cyanide and iron carbide, FeC_2 (Chapter XIII., Note 12). Oxidising substances change it into potassium ferricyanide. With strong sulphuric acid it gives carbonic oxide, and with dilute sulphuric acid, when heated, prussic acid is evolved according to the equation: $2K_4FeC_6N_6 + 3H_2SO_4 = K_2Fe_2C_6N_6 + 3K_2SO_4 + 6HCN$; hence in the yellow prussiate K_2 replaces Fe.

the metals of the alkalis and alkaline earths ; these are readily soluble, have a neutral reaction, and resemble the yellow prussiate. Solutions of these salts form precipitates with the salts of other metals, because the ferrocyanides of the heavy metals are insoluble. Here either the whole of the potassium of the yellow prussiate, or only a part of it, is exchanged for an equivalent quantity of the heavy metal. Thus, when a cupric salt is added to a solution of yellow prussiate, a red precipitate is obtained which still contains half the potassium of the yellow prussiate :

$$K_4FeC_6N_6 + CuSO_4 = K_2CuFeC_6N_6 + K_2SO_4.$$

But if the process be reversed (the salt of copper being then in excess) the whole of the potassium will be exchanged for copper, forming a reddish-brown precipitate, $Cu_2FeC_6N_6,9H_2O$. This reaction and those similar to it are very sensitive and may be used for detecting metals in solution, more especially as the colour of the precipitate very often shows a marked difference when one metal is exchanged for another. Zinc, cadmium, lead, antimony, tin, silver, cuprous and aurous salts form *white* precipitates ; cupric, uranium, titanium and molybdenum salts *reddish-brown* ; those of nickel, cobalt, and chromium, *green* precipitates ; *with ferrous salts*, ferrocyanide forms, as has been already mentioned, a *white* precipitate—namely, $Fe_2FeC_6N_6$, or FeC_3N_3—which turns blue on exposure to air, and with ferric salts a *blue precipitate* called *Prussian blue*. Here the potassium is replaced by iron, the reaction being expressed thus : $2Fe_2Cl_6 + 3K_4FeC_6N_6 = 12KCl + Fe_4Fe_3C_{18}N_{18}$, the latter formula expressing the composition of Prussian blue. It is therefore the compound $4Fe(CN)_3 + 3Fe(CN)_2$. The yellow prussiate is prepared in chemical works on a large scale especially for the manufacture of this blue pigment, which is used for dyeing cloth and other fabrics and also as one of the ordinary blue paints. It is insoluble in water, and the stuffs are therefore dyed by first soaking them in a solution of a ferric salt and then in a solution of yellow prussiate. If however an excess of yellow prussiate be present complete substitution between potassium and iron does not occur, and *soluble Prussian blue* is formed ; $KFe_2(CN)_6 = KCN,Fe(CN)_2,Fe(CN)_3$. This blue salt is colloidal, is soluble in pure water, but insoluble and precipitated when other salts—for instance, potassium or sodium chloride—are present even in small quantities, and is therefore first obtained as a precipitate.[29]

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[29] Skraup obtained this salt both from potassium ferrocyanide with ferric chloride and from ferricyanide with ferrous chloride, which evidently shows that it contains iron

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Potassium ferricyanide, or *red prussiate* of potash, $K_3FeC_6N_6$, is called 'Gmelin's salt,' because this savant obtained it by the action of chlorine on a solution of the yellow prussiate: $K_4FeC_6N_6 + Cl = K_3FeC_6N_6 + KCl$. The reaction is due to the ferrous salt being changed by the action of the chlorine into a ferric salt. It separates from solutions in anhydrous, well-formed prisms of a red colour, but the solution has an olive colour; 100 parts of water, at 10°, dissolve 37 parts of the salt, and at 100°, 78 parts.[30] The red prussiate gives a blue precipitate with ferrous salts, called *Turnbull's blue*, very much like Prussian blue (and the soluble variety), because it also contains ferrous cyanide and ferric cyanide, although in another propor-

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in both the ferric and ferrous states. With ferrous chloride it forms Prussian blue, and with ferric chloride Turnbull's blue.

Prussian blue was discovered in the beginning of the last century by a Berlin manufacturer, Diesbach. It was then prepared, as it sometimes is also at present, directly from potassium cyanide obtained by heating animal charcoal with potassium carbonate. The mass thus obtained is dissolved in water, alum is added to the solution in order to saturate the free alkali, and then a solution of green vitriol is added which has previously been sufficiently exposed to the air to contain both ferric and ferrous salts. If the solution of potassium cyanide be mixed with a solution containing both salts, Prussian blue will be formed, because it is a compound of ferrous cyanide, FeC_2N_2, and ferric cyanide, $Fe_2C_6N_6$. A ferric salt with potassium ferrocyanide forms a blue colour, because ferrous cyanide is obtained from the first salt and ferric cyanide from the second. During the preparation of this compound alkali must be avoided, as otherwise the precipitate would contain oxides of iron. Prussian blue has not a crystalline structure; it forms a blue mass with a copper-red metallic lustre. Both acids and alkalis act on it. The action is at first confined to the ferric salt it contains. Thus alkalis form ferric oxide and ferrocyanide in solution: $2Fe_2C_6N_6,3FeC_2N_2 + 12KHO = 2(Fe_2O_3,3H_2O) + 3K_4FeC_6N_6$. Various ferrocyanides may thus be prepared. Prussian blue is soluble in an aqueous solution of oxalic acid, forming blue ink. In air, when exposed to the action of light, it fades; but in the dark again absorbs oxygen and becomes blue, which fact is also sometimes noticed in blue cloth. An excess of potassium ferrocyanide renders Prussian blue soluble in water, although insoluble in various saline solutions—that is, it converts it into the soluble variety. Strong hydrochloric acid also dissolves Prussian blue.

[30] An excess of chlorine must not be employed in preparing this compound, otherwise the reaction goes further. It is easy to find out when the action of the chlorine on potassium ferrocyanide must cease; it is only necessary to take a sample of the liquid and add a solution of a ferric salt to it. If a precipitate of Prussian blue is formed, more chlorine must be added, as there is still some undecomposed ferrocyanide, for the ferricyanide does not give a precipitate with ferric salts. Potassium ferricyanide, like the ferrocyanide, easily exchanges its potassium for hydrogen and various metals by double decomposition. With the salts of tin, silver, and mercury it forms yellow precipitates, and with those of uranium, nickel, cobalt, copper, and bismuth brown precipitates. The lead salt under the action of sulphuretted hydrogen forms lead sulphide and a hydrogen salt or acid, $H_3FeC_6N_6$, corresponding with potassium ferricyanide, which is soluble, crystallises in red needles, and resembles hydroferrocyanic acid, $H_4FeC_6N_6$. Under the action of reducing agents—for instance, sulphuretted hydrogen, copper—potassium ferricyanide is changed into ferrocyanide, especially in the presence of alkalis, and thus forms a rather energetic *oxidising agent*—capable, for instance, of changing manganous oxide into dioxide, bleaching tissues, &c.

tion, being formed according to the equation: $3FeCl_2+2K_3FeC_6N_6=6KCl+Fe_3Fe_2C_{12}N_{12}$, or $3FeC_2N_2,Fe_2C_6N_6$; in Prussian blue we have Fe_7Cy_{18}, and here Fe_5Cy_{12}. A ferric salt ought to form ferric cyanide $Fe_2C_6N_6$, with red prussiate, but ferric cyanide is soluble, and therefore no precipitate is obtained, and the liquid only becomes brown.[31]

If chlorine and sodium are representatives of independent groups of elements, the same may also be said of iron. Its nearest analogues show, besides a similarity in character, a likeness as regards physical properties and a proximity in atomic weight. Iron occupies a medium position amongst its nearest analogues, both with respect to properties and faculty of forming saline oxides, and also as regards atomic weight. On the one hand, cobalt, 58, and nickel, 59, approach iron, 56; they are metals of a more basic character, they do not form stable acids or higher degrees of oxidation, and are a transition to copper, 63, and zinc, 65. On the other hand, manganese, 55, and chromium, 52, are the nearest to iron; they form both basic and acid oxides, and are a transition to the metals possessing acid properties. In addition to having atomic weights approximately alike, chromium, manganese, iron, cobalt, nickel, and copper have also nearly the same specific gravity, so that the atomic volumes and the molecules of their analogous compounds are also near to one another (see table at the beginning of this volume). Besides this, the likeness between the above-mentioned elements is also seen from the following:

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[31] It is important to mention a series of readily crystallisable salts formed by the action of nitric acid on potassium and other ferrocyanides and ferricyanides. These salt contain the elements of nitric oxide, and are therefore called *nitro-(nitroso) ferricyanides* (*nitroprussides*). Generally a crystalline sodium salt is obtained, $Na_2FeC_5N_6O,2H_2O$. In its composition this salt differs from the red sodium salt, $Na_3FeC_6N_6$, by the fact that in it one molecule of sodium cyanide, NaCN, is replaced by nitric oxide, NO. In order to prepare it, potassium ferrocyanide in powder is mixed with five-sevenths of its weight of nitric acid diluted with an equal volume of water. The mixture is at first left at the ordinary temperature, and then heated on a water-bath. Here ferricyanide is first of all formed (as shown by the liquid giving a precipitate with ferrous chloride), which then disappears (no precipitate with ferrous chloride), and forms a green precipitate. The liquid, when cooled, deposits crystals of nitre. The liquid is then strained off and mixed with sodium carbonate, boiled, filtered, and evaporated; sodium nitrate and the salt described are deposited in crystals. It separates in prisms of a red colour. Alkalis and salts of the alkaline earths do not give precipitates: they are soluble, but the salts of iron, zinc, copper, and silver form precipitates where sodium is exchanged with these metals. It is remarkable that the sulphides of the alkali metals give with this salt an intense bright purple coloration. This series of compounds was discovered by Gmelin and studied by Playfair and others (1849).

This series to a certain extent resembles the nitro-sulphide series described by Roussin. Here the primary compound consists of black crystals, which are obtained as follows:—Solutions of potassium hydrosulphide and nitrate are mixed, and the mixture is agitated whilst ferric chloride is added, then boiled and filtered; on cooling, *black crystals* are deposited, having the composition $Fe_6S_5(NO)_{10},H_2O$ (Rosenberg), or, according to Demel, $FeNO_2,NH_4S$. They have a slightly metallic lustre, and are soluble in water, alcohol, and ether. They absorb the latter as easily as calcium chloride absorbs water. In the presence of alkalis these crystals remain unchanged, but with acids they evolve nitric oxides. There are several compounds which are capable of interchanging, and correspond with Roussin's salt. Here we enter into the series of the nitrogen compounds which have been as yet but little investigated, and will most probably in time form most instructive material for studying the nature of that element. These series of compounds are as unlike the usual saline compounds of inorganic chemistry as are organic hydrocarbons. There is no necessity to describe these series in detail, because their connection with other compounds is not yet clear, and they have not yet any application.

They form suboxides, RO, fairly energetic bases, isomorphous with magnesia—for instance, the salt $RSO_4,7H_2O$, akin to $MgSO_4,7H_2O$, and $FeSO_4,7H_2O$, or to sulphates containing less water; with alkali sulphates all form double salts crystallising with $6H_2O$; all are capable of forming ammonium salts, &c. The lower oxides, in the cases of nickel and cobalt, are tolerably stable, are not easily oxidised (the nickel compound with more difficulty than cobalt, a transition to copper); with manganese, and especially with chromium, they are more easily oxidised than with iron and pass into higher oxides. They also form oxides of the form R_2O_3, and with nickel, cobalt, and manganese this oxide is very unstable, and is more easily reduced than ferric oxide; but, in the case of chromium, it is very stable, and forms the ordinary kind of salts. It is isomorphous with ferric oxide, forms alums, is a feeble base, &c. Chromium, manganese, and iron are oxidised by alkali and oxidising agents, forming salts like Na_2SO_4; but cobalt and nickel are difficult to oxidise; their acids are not known with any certainty, and are, in all probability, still less stable than the ferrates. Cr, Mn and Fe form compounds R_2Cl_6 which are like Fe_2Cl_6 in many respects; in Co this faculty is weaker and in Ni it has almost disappeared. The cyanogen compounds, especially of manganese and cobalt, are very near akin to the corresponding ferrocyanides. The oxides of nickel and cobalt are more easily reduced to metal than those of iron, but those of manganese and chromium are not reduced so easily as iron, and the metals themselves are not easily obtained in a pure state; they are capable of forming varieties resembling cast iron. The metals Cr, Mn, Fe, Co, and Ni have a grey iron colour and are very difficult to melt, but nickel and cobalt can be melted in the reverberatory furnace and are more fusible than iron, whilst chromium is more difficult to melt than platinum (Deville). These metals decompose water, but with greater difficulty as the atomic weight rises, forming a transition to copper, which does not decompose water. All the compounds of these metals have various colours, which are sometimes very bright, especially in the higher stages of oxidation.

These metals of the iron group are often met with together in nature. Manganese nearly everywhere accompanies iron, and iron is always an ingredient in the ores of manganese. Chromium is found principally as chrome ironstone—that is, a peculiar kind of magnetic oxide in which Fe_2O_3 is replaced by Cr_2O_3.

Nickel and cobalt are as inseparable companions as iron and manganese. The similarity between them even extends to such remote properties as magnetic qualities. In this series of metals we find those which are the most magnetic: iron, cobalt, and nickel. There is even a magnetic oxide among the chromium compounds, such being unknown in the other series. Nickel easily becomes passive in strong nitric acid. It absorbs hydrogen in just the same way as iron. In short, in the series Cr, Mn, Fe, Co, and Ni, there are many points in common although there are many differences, as will be seen still more clearly on becoming acquainted with cobalt and nickel.

In nature *cobalt* is principally found in combination with arsenic and sulphur. *Cobalt arsenide*, or *cobalt speiss*, $CoAs_2$, is found in brilliant crystals of the regular system, principally in Saxony. *Cobalt glance*, $CoAs_2CoS_2$, resembles it very much, and also belongs to the regular system; it is found in Sweden, Norway, and the Caucasus. *Kupfernickel* is a nickel ore in combination with arsenic, but of a different composition from cobalt arsenide, having the formula NiAs; it is found in Bohemia and Saxony. It has a copper-red colour and is rarely crystalline; it is so called because the miners of Saxony first mistook it for an ore of copper (*Kupfer*), but were unable to extract copper from it. *Nickel glance*, $NiS_2,NiAs_2$, corresponding with cobalt glance, is also known. Nickel accompanies the ores of cobalt and cobalt those of nickel, so that both metals are found together. The ores of cobalt are worked in the Caucasus in the Government of Elizavetopolsk. Nickel ores containing aqueous hydrated nickel silicate are found in the Ural (Revdansk). Large quantities of a similar ore are exported into Europe from New Caledonia. Both ores contain about 12 per cent. Ni. *Garnierite*, $(RO)_5(SiO_2)_4 1\frac{1}{2}H_2O$, where R=Ni and Mg, predominates in the New Caledonian ore. Large deposits of nickel have been discovered in Canada, where the ore (as nickelous pyrites) is free from arsenic. Cobalt is principally worked up into cobalt compounds, but nickel is generally reduced to the metallic state, in which it is now often used for alloys—for instance, for coinage in many European States, and for plating other metals, because it does not oxidise. Cobalt arsenide and cobalt glance are principally used for the preparation of cobalt compounds; they are first sorted by discarding the rocky matter, and then roasted. During this process most of the sulphur and arsenic disappears; the arsenious anhydride volatilises with the sulphurous anhydride and the metal also oxidises.[52] It is a simple matter to obtain nickel and cobalt from their oxides. In order to obtain the latter, solutions of their salts are treated with sodium carbonate and the precipitated carbonates are heated; the suboxides are thus obtained, and these latter are reduced in a stream of hydrogen, or even by heating with ammonium chloride. They easily oxidise when in the state of powder. When the chlorides of nickel and cobalt are heated in a stream of hydrogen, the metal is deposited in brilliant scales. *Nickel is always much more easily and quickly reduced than cobalt.* Nickel melts more easily than cobalt, and this even furnishes a means of testing the heating powers of a reverberatory furnace. Cobalt fuses at a temperature only a little lower than that at which iron does. In general, cobalt is nearer to iron than nickel, nickel being nearer to copper.[32 bis] Both nickel and cobalt have magnetic properties like iron, but Co is less magnetic than Fe, and Ni still less so. The specific gravity of nickel reduced by hydrogen is 9·1 and that of cobalt 8·9. Fused cobalt has a specific gravity of 8·5, the density of ordinary nickel being almost the same. Nickel has a greyish, silvery-white colour; it is brilliant and very ductile, so that the finest wire may be easily drawn from it. This wire has a resistance to tension equal to iron wire. The beautiful colour of nickel, and the high polish which it is capable of receiving and retaining, as it does not oxidise, render it a useful metal for many purposes, and in many ways it resembles silver.[32 tri] It is now very common to cover

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[52] The residue from the roasting of cobalt ores is called *safflor*, and is often met with in commerce. From this the purer compounds of cobalt may be prepared. The ores of nickel are also first roasted, and the oxides dissolved in acid, nickelous salts being then obtained.

The further treatment of cobalt and nickel ores is facilitated if the arsenic can be almost entirely removed, which may be effected by roasting the ore a second time with a small addition of nitre and sodium carbonate; the nitre combines with the arsenic, forming an arsenious salt, which may be extracted with water. The remaining mass is dissolved in hydrochloric acid, mixed with a small quantity of nitric acid. Copper, iron, manganese, nickel, cobalt, &c., pass into solution. By passing hydrogen sulphide through the solution, copper, bismuth, lead, and arsenic are deposited as metallic sulphides; but iron, cobalt, nickel, and manganese remain in solution. If an alkaline solution of bleaching powder be then added to the remaining solution, the whole of the manganese will first be deposited in the form of dioxide, then the cobalt as hydrated cobaltic oxide, and finally the nickel also. It is, however, impossible to rely on this method for effecting a complete separation, the more so since the higher oxides of the three above-mentioned metals have all a black colour; but, after a few trials, it will be easy to find how much bleaching powder is required to precipitate the manganese, and the amount which will precipitate all the cobalt. The manganese may also be separated from cobalt by precipitation from a mixture of the solutions of both metals (in the form of the 'ous' salts) with ammonium sulphide, and then treating the precipitate with acetic acid or dilute hydrochloric acid, in which manganese sulphide is easily soluble and cobalt sulphide almost insoluble. Further particulars relating to the separation of cobalt from nickel may be found in treatises on analytical chemistry. In practice it is usual to rely on the rough method of separation founded on the fact that nickel is more easily reduced and more difficult to oxidise than cobalt. The New Caledonian ore is smelted with $CaSO_4$ and $CaCO_3$ on coke, and a metallic regulus is obtained containing all the Ni, Fe, and S. This is roasted with SiO_2, which converts all the iron into slag, whilst the Ni remains combined with the S; this residue on further roasting gives NiO, which is reduced by the carbon to metallic Ni. The Canadian ore (a pyrites containing 11 p. c. Ni) is frequently treated in America (after a preliminary dressing) by smelting it with Na_2SO_4 and charcoal; the resultant fusible Na_2S then dissolves the CuS and FeS_2, while the NiS is obtained in a bottom layer (Bartlett and Thomson's process) from which Ni is obtained in the manner described above.

For manufacturing purposes somewhat impure cobalt compounds are frequently used, which are converted into *smalt*. This is glass containing a certain amount of cobalt oxide; the glass acquires a bright blue colour from this addition, so that when powdered it may be used as a blue pigment; it is also unaltered at high temperatures, so that it used to take the place now occupied by Prussian blue, ultramarine, &c. At present smalt is almost exclusively used for colouring glass and china. To prepare smalt, ordinary impure cobalt ore (zaffre) is fused in a crucible with quartz and potassium carbonate. A fused mass of cobalt glass is thus formed, containing silica, cobalt oxide, and potassium oxide, and a metallic mass remains at the bottom of the crucible, containing almost all the other metals, arsenic, nickel, copper, silver, &c. This metallic mass is called *speiss*, and is used as nickel ore for the extraction of nickel. Smalt usually contains 70 p.c. of silica, 20 p.c. of potash and soda, and about 5 to 6 p.c. of cobaltous oxide; the remainder consisting of other metallic oxides.

[32 bis] All we know respecting the relations of Co and Ni to Fe and Cu confirms the fact that Co is more closely related to Fe and Ni to Cu; and as the atomic weight of Fe = 56 and of Cu = 63, then according to the principles of the periodic system it would be expected that the atomic weight of Co would be about 58–60, whilst that of Ni should be greater than that of Co but less than that of Cu, *i.e.* about 59·5 – 60·5. However, as yet the majority of the determinations of the atomic weights of Co and Ni give a different result and show that a lower atomic weight is obtained for Ni than for Co. Thus K. Winkler (1894) obtained (employing metals deposited electrolytically and determining the amount of iodine which combined with them) Ni = 58·72 and Co = 59·37 (if H = 1 and I = 126·53). In my opinion this should not be regarded as proving that the principles of the periodic system cannot be applied in this instance, nor as a reason for altering the position of these elements in the system (*i.e.* by placing Ni after Fe, and Co next to Cu), because in the first place the figures given by different chemists (for instance, Zimmermann, Krüss, and others) are somewhat divergent, and in the second place the majority of the latest modes of determining the atomic weights of Co and Ni aim at finding what weights of these metals react with known weights of other elements without taking into account the faculty they have of absorbing hydrogen; since this faculty is more developed in Ni than in Co the hydrogen (occluded in Ni) should lower the atomic weight of Ni more than that of Co. On the whole, the question of the atomic weights of Co and Ni cannot yet be considered as decided, notwithstanding the numerous researches which have been made; still there can be no doubt that the atomic weights of these two metals are very nearly equal, and greater than that of Fe, but less than that of Cu. This question is of great interest, not only for completing our knowledge of these metals, but also for perfecting our knowledge of the periodic system of the elements.

[32 tri] For instance, the alkalis may be fused in nickel vessels as well as in silver, because they have no action upon either metal. Nickel, like silver, is not acted upon by

other metals with a layer of nickel (nickel plating). This is done by a process of electro-plating, using a solution of a nickel salt. The colour of cobalt is dark and redder; it is also ductile, and has a greater tensile resistance than iron. Dilute acids act very slowly on nickel and cobalt; nitric acid may be considered as the best solvent for them. The solutions in every case contain salts corresponding with the ferrous salts—that is, the *salts* CoX_2, NiX_2, *correspond with the suboxides* of these metals. These salts in their types are similar to the magnesium salts. The salts of nickel when crystallising with water have a green colour, and form bright green solutions, but in the anhydrous state they most frequently have a yellow colour. The salts of cobalt are generally rose-coloured, and generally blue when in the anhydrous state. Their aqueous solutions are rose-coloured. Cobaltous chloride is easily soluble in alcohol, and forms a solution of an intense blue colour.[33]

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dilute acids. Only nitric acid dissolves both metals well. Nickel is harder, and fuses at a higher temperature than silver. For castings, a small quantity of magnesium (0·001 part by weight) is added to nickel to render it more homogeneous (just as aluminium is added to steel). Nickel forms many valuable alloys. Steel containing 8 p.c. Ni is particularly valuable, its limit of elasticity is higher and its hardness is greater; it is used for armour plate and other large pieces. The alloys of nickel, especially with copper and zinc (melchior, see later), aluminium and silver, although used in certain cases, are now replaced by nickel-plated or nickel-deposited goods (deposited by electricity from a solution of the ammonium salts).

[33] The change of colour is dependent in all probability on the combination with water, or according to others on polymeric transformation. It enables a solution of cobalt chloride to be used as sympathetic ink. If something be written with cobalt chloride on white paper, it will be invisible on account of the feeble colour of the solution, and when dry nothing can be distinguished. If, however, the paper be heated before the fire, the rose-coloured salt will be changed into a less hydrous blue salt, and the writing will become quite visible, but fade away when cool.

The change of colour which takes place in solutions of $CoCl_2$ under the influence not only of solution in water or alcohol, but also of a change of temperature, is a characteristic of all the halogen salts of cobalt. Crystalline iodide of cobalt, CoI_26H_2O, gives a dark red solution between −22° and +20°; above +20° the solution turns brown and passes from olive to green, from +85° to 820° the solution remains green. According to Étard the change of colour is due to the fact that at first the solution contains the hydrate CoI_2H_2O, and that above 85° it contains CoI_24H_2O. These hydrates can be crystallised from the solutions; the former at ordinary temperature and the latter on heating the solution. The intermediate olive colour of the solutions corresponds to the incipient decomposition of the hexahydrated salt and its passage into CoI_24H_2O. A solution of the hexahydrated chloride of cobalt, $CoCl_26H_2O$, is rose-coloured between −22° and +25°; but the colour changes starting from +25°, and passes through all the tints between red and blue right up to 50°; a true blue solution is only obtained at 55° and remains up to 800°. This true blue solution contains another hydrate, $CoCl_22H_2O$.

The dependence between the solubility of the iodide and chloride of cobalt and he temperature is expressed by two almost straight lines corresponding to the hexa- and di-hydrates; the passage of the one into the other hydrate being expressed by a curve. The same character of phenomena is seen also in the variation of the vapour

If a solution of potassium hydroxide be added to a solution of a cobalt salt, a blue precipitate of the basic salt will be formed. If a

tension of solutions of chloride of cobalt with the temperature. We have repeatedly seen that aqueous solutions (for instance, Chapter XXII., Note 28 for Fe_2Cl_6) deposit different crystallo-hydrates at different temperatures, and that the amount of water in the hydrate decreases as the temperature *t* rises, so that it is not surprising that $CoCl_2 2H_2O$ (or according to Potilitzin $CoCl_2H_2O$) should separate out above 55° and $CoCl_2 6H_2O$ at 25° and below. Nor is it exceptional that the colour of a salt varies according as it contains different amounts of H_2O. But in this instance it is characteristic that the change of colour takes place in solution in the presence of an excess of water. This apparently shows that the actual solution may contain either $CoCl_2 6H_2O$ or $CoCl_2 2H_2O$ And as we know that a solution may contain both metaphosphoric PHO_3 and orthophosphoric acid $H_3PO_4 = HPO_3 + H_2O$, as well as certain other anhydrides, the question of the state of substances in solutions becomes still more complicated.

Nickel sulphate crystallises from neutral solutions at a temperature of from 15° to 20° in *rhombic* crystals containing $7H_2O$. Its form approaches very closely to that of the salts of zinc and magnesium. The planes of a vertical prism for magnesium salts are inclined at an angle of 90° 30′, for zinc salts at an angle of 91° 7′, and for nickel salts at an angle of 91° 10′. Such is also the form of the zinc and magnesium selenates and chromates. Cobalt sulphate containing 7 molecules of water is deposited in crystals of the *monoclinic* system, like the corresponding salts of iron and manganese. The angle of a vertical prism for the iron salt = 82° 20′, for cobalt = 82° 22′, and the inclination of the horizontal pinacoid to the vertical prism for the iron salt = 99° 2′, and for the cobalt salt 99° 36′ All the isomorphous mixtures of the salts of magnesium, iron, cobalt, nickel and manganese have the same form if they contain 7 mol. H_2O and iron or cobalt predominate, whilst if there is a preponderance of magnesium, zinc, or nickel, the crystals have a rhombic form like magnesium sulphate. Hence these sulphates are *dimorphous*, but for some the one form is more stable and for others the other. Brooke, Moss, Mitscherlich, Rammelsberg, and Marignac have explained these relations. Brooke and Mitscherlich also supposed that $NiSO_4,7H_2O$ is not only capable of assuming these forms, but also that of the *tetragonal* system, because it is deposited in this form from acid, and especially from slightly-heated solutions (30° to 40°). But Marignac demonstrated that the tetragonal crystals do not contain 7, but 6, molecules of water, $NiSO_4,6H_2O$. He also observed that a solution evaporated at 50° to 70° deposits monoclinic crystals, but of a different form from ferrous sulphate, $FeSO_4,7H_2O$—namely, the angle of the prism is 71° 52′, that of the pinacoid 95° 6′. This salt appears to be the same with 6 molecules of water as the tetragonal. Marignac also obtained magnesium and zinc salts with 6 molecules of water by evaporating their solutions at a higher temperature, and these salts were found to be isomorphous with the monoclinic nickel salt. In addition to this it must be observed that the rhombic crystals of nickel sulphate with $7H_2O$ become turbid under the influence of heat and light, lose water, and change into the tetragonal salt. The monoclinic crystals in time also become turbid, and change their structure, so that the tetragonal form of this salt is the most stable. Let us also add that nickel sulphate in all its shapes forms very beautiful emerald green crystals, which, when heated to 280°, assume a dirty greenish-yellow hue and then contain one molecule of water.

Klobb (1891) and Langlot and Lenoir obtained anhydrous $CoSO_4$ and $NiSO_4$ by igniting the hydrated salt with $(NH_4)_2SO_4$ until the ammonium salt had completely volatilised and decomposed.

We may add that when equivalent aqueous solutions of NiX_2 (green) and CoX_2 (red) are mixed together they give an almost colourless (grey) solution, in which the green and red colour of the component parts disappears owing to the combination of the complementary colours.

A double salt $NiKF_3$ is obtained by heating $NiCl_2$ with KFHF in a platinum crucible; $KCoF_3$ is formed in a similar manner. The nickel salt occurs in fine green plates, easily air be not completely excluded during the precipitation by boiling, the precipitate will also contain brown cobaltic hydroxide formed by the further oxidation of the cobaltous oxide.[34] Under similar circumstances nickel salts form *a green precipitate of nickelous hydroxide*, the formation of which is not hindered by the presence of ammonium salts, but in that case only requires more alkali to completely separate the nickel. The nickelous oxide obtained by heating the hydroxide, or from the carbonate or nitrate, is a grey powder, easily soluble in acids and easily reduced, but the same substance may be obtained in the crystalline form as an ordinary product from the ores; it crystallises in regular octahedra, with a metallic lustre, and is of a grey colour. In this state the nickelous oxide almost resists the action of acids.[34 bis]

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soluble in water but scarcely soluble in ethyl and methyl alcohol. They decompose into green oxide of nickel and potassium fluoride when heated in a current of air. The analogous salt of cobalt crystallises in crimson flakes.

If instead of potassium fluoride, $CoCl_2$ or $NiCl_2$ be fused with ammonium fluoride, they also form double salts with the latter. This gives the possibility of obtaining anhydrous fluorides NiF_2 and CoF_2. Crystalline fluoride of nickel, obtained by heating the amorphous powder formed by decomposing the double ammonium salt in a stream of hydrofluoric acid, occurs in beautiful green prisms, sp. gr. 4·63, which are insoluble in water, alcohol, and ether; sulphuric, hydrochloric, and nitric acids also have no action upon them, even when heated; NiF_2 is decomposed by steam, with the formation of black oxide, which retains the crystalline structure of the salt. Fluoride of cobalt, obtained as a rose-coloured powder by decomposing the double ammonium salt with the aid of heat in a stream of hydrofluoric acid, fuses into a ruby-coloured mass which bears distinct signs of a crystalline structure; sp. gr. 4·43. The molten salt only volatilises at about 1400°, which forms a clear distinction between CoF_2 and the volatile NiF_2. Hydrochloric, sulphuric, and nitric acids act upon CoF_2 even in the cold, although slowly, while when heated the reaction proceeds rapidly (Poulenc, 1892).

[34] Hydrated suboxide of cobalt (de Schulten, 1889) is obtained in the following manner. A solution of 10 grams of $CoCl_2 6H_2O$ in 60 c.c. of water is heated in a flask with 250 grams of caustic potash and a stream of coal gas is passed through the solution. When heated the hydrate of the suboxide of cobalt which separates out, dissolves in the caustic potash and forms a dark blue solution. This solution is allowed to stand for 24 hours in an atmosphere of coal gas (in order to prevent oxidation). The crystalline mass which separates out has a composition $Co(OH)_2$, and to the naked eye appears as a violet powder, which is seen to be crystalline under the microscope. The specific gravity of this hydrate is 3·597 at 15°. It does not undergo change in the air; warm acetic acid dissolves it, but it is insoluble in warm and cold solutions of ammonia and sal-ammoniac.

[34 bis] The following reaction may be added to those of the cobaltous and nickelous salts: potassium cyanide forms a precipitate with cobalt salts which is soluble in an excess of the reagent and forms a green solution. On heating this and adding a certain quantity of acid, a double *cobalt cyanide* is formed which corresponds with potassium ferricyanide. Its formation is accompanied with the evolution of hydrogen, and is founded upon the property which cobalt has of oxidising in an alkaline solution, the development of which has been observed in such a considerable measure in the cobaltamine salts. The process which goes on here may be expressed by the following equation:

It is interesting to note *the relation* of the cobaltous and nickelous hydroxides *to ammonia* ; aqueous ammonia dissolves the precipitate of cobaltous and nickelous hydroxide. The blue ammoniacal solution of nickel resembles the same solution of cupric oxide, but has a somewhat reddish tint. It is characterised by the fact that it dissolves silk in the same way as the ammoniacal cupric oxide dissolves cellulose. Ammonia likewise dissolves the precipitate of cobaltous hydroxide, forming a brownish liquid, which becomes darker in air and finally assumes a bright red hue, absorbing oxygen. The admixture of ammonium chloride prevents the precipitation of cobalt salts by ammonia ; when the ammonia is added, a brown solution is obtained from which, as in the case of the preceding solution, potassium hydroxide does not separate the cobaltous oxide. Peculiar compounds are produced in this solution ; they are comparatively stable, containing ammonia and an excess of oxygen ; they bear the name cobaltoamine and cobaltiamine salts. They have been principally investigated by Genth, Frémy, Jörgenson and others. Genth found that when a cobalt salt, mixed with an excess of ammonium chloride, is treated with ammonia and exposed to the air, after a certain lapse of time, on adding hydrochloric acid and boiling, a red powder is precipitated and the remaining solution contains an orange salt. The study of these compounds led to the discovery of a whole series of similar salts, some of which correspond with particular higher degrees of oxidation of cobalt, which are described later.[35]

CoC_2N_2+4KCN first forms $CoK_4C_6N_6$, which salt with water, H_2O, forms potassium hydroxide, KHO, hydrogen, H, and the salt, $K_3CoC_6N_6$. Here naturally the presence of the acid is indispensable in consequence of its being required to combine with the alkali. From aqueous solutions this salt crystallises in transparent, hexagonal prisms of a yellow colour, easily soluble in water. The reactions of double decomposition, and even the formation of the corresponding acid, are here completely the same as in the case of the ferricyanide. If a nickelous salt be treated in precisely the same manner as that just described for a salt of cobalt, decomposition will occur.

[35] The cobalt salts may be divided into at least the following classes, which repeat themselves for Cr, Ir, Rh (we shall not stop to consider the latter, particularly as they closely resemble the cobalt salts) :—

(*a*) *Ammonium cobalt salts*, which are simply direct compounds of the cobaltous salts CoX_2 with ammonia, similar to various other compounds of the salts of silver, copper, and even calcium and magnesium, with ammonia. They are easily crystallised from an ammoniacal solution, and have a pink colour. Thus, for instance, when cobaltous chloride in solution is mixed with sufficient ammonia to redissolve the precipitate first formed, octahedral crystals are deposited which have a composition $CoCl_2,H_2O,6NH_3$. These salts are nothing else but combinations with ammonia of crystallisation—if it may be so termed—likening them in this way to combinations with water of crystallisation. This similarity is evident both from their composition and from their capability of giving off ammonia at various temperatures. The most important point to observe is that all these salts contain 6 molecules of ammonia to 1 atom of cobalt, and this ammonia is held in fairly stable connection. Water decomposes these salts. (Nickel behaves similarly without forming other compounds corresponding to the true cobaltic.)

(*b*) The solutions of the above-mentioned salts are rendered turbid by the action of

Nickel does not possess this property of absorbing the oxygen of the air when in an ammoniacal solution. In order to understand this distinc-

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the air; they absorb oxygen and become covered with a crust of *oxycobaltamine salts.* The latter are sparingly soluble in aqueous ammonia, have a brown colour, and are characterised by the fact that with warm water *they evolve oxygen,* forming salts of the following category: The nitrate may be taken as an example of this kind of salt; its composition is $CoN_2O_7,5NH_3,H_2O$. It differs from cobaltous nitrate, $Co(NO_3)_2$, in containing an extra atom of oxygen—that is, it corresponds with cobalt dioxide, CoO_2, in the same way that the first salts correspond with cobaltous oxide; they contain 5, and not 6, molecules of ammonia, as if NH_3 had been replaced by O, but we shall afterwards meet compounds containing either $5NH_3$ or $6NH_3$ to each atom of cobalt.

(*c*) *The luteocobaltic salts* are thus called because they have a yellow (luteus) colour. They are obtained from the salts of the first kind by submitting them in dilute solution to the action of the air; in this case salts of the second kind are not formed, because they are decomposed by an excess of water, with the evolution of oxygen and the formation of luteocobaltic salts. By the action of ammonia the salts of the fifth kind (roseocobaltic) are also converted into luteocobaltic salts. These last-named salts generally crystallise readily, and have a yellow colour; they are comparatively much more stable than the preceding ones, and even for a certain time resist the action of boiling water. Boiling aqueous potash liberates ammonia and precipitates hydrated cobaltic oxide, $Co_2O_3,8H_2O$, from them. This shows that the luteocobaltic salts correspond with cobaltic oxide, Co_2O_3, and those of the second kind with the dioxide. When a solution of luteocobaltic sulphate, $Co_2(SO_4)_3,12NH_3,4H_2O$, is treated with baryta, barium sulphate is precipitated, and the solution contains luteocobaltic hydroxide, $Co(OH)_3,6NH_3$, which is soluble in water, is powerfully alkaline, absorbs the oxygen of the air, and when heated is decomposed with the evolution of ammonia. This compound therefore corresponds to a solution of cobaltic hydroxide in ammonia. The luteocobaltic salts contain 2 atoms of cobalt and 12 molecules of ammonia—that is, $6NH_3$ to each atom of cobalt, like the salts of the first kind. The CoX_2 salts have a metallic taste, whilst those of luteocobalt and others have a purely saline taste, like the salts of the alkali metals. In the luteo-salts all the X's react (are ionised, as some chemists say) as in ordinary salts—for instance, all the Cl_3 is precipitated by a solution of $AgNO_3$; all the $(SO_4)_3$ gives a precipitate with BaX_2, &c. The double salt formed with $PtCl_4$ is composed in the same manner as the potassium salt, $K_2PtCl_4 = 2KCl + PtCl_4$, that is, contains $(CoCl_3,6NH_3)_2,3PtCl_4$, or the amount of chlorine in the $PtCl_4$ is double that in the alkaline salt. In the roseopentamine (*e*), and roseotetramine (*f*), salts, also all the X's react or are ionised, but in the (*g*) and (*h*) salts only a portion of the X's react, and they are equal to the (*e*) and (*f*) salts minus water; this means that although the water dissolves them it is not combined with them, as PHO_3 differs from PH_3O_3; phenomena of this class correspond exactly to what has been already (Chapter XXI., Note 7) mentioned respecting the green and violet salts of oxide of chromium.

(*d*) *The fuscocobaltic salts.* An ammoniacal solution of cobalt salts acquires a brown colou in the air, due to the formation of these salts. They are also produced by the decomposition of salts of the second kind; they crystallise badly, and are separated from their solutions by addition of alcohol or an excess of ammonia. When boiled they give up the ammonia and cobaltic oxide which they contain. Hydrochloric and nitric acids give a yellow precipitate with these salts, which turns red when boiled, forming salts of the next category. The following is an example of the composition of two of the fuscocobaltic salts, $Co_2O(SO_4)_2,8NH_3,4H_2O$ and $Co_2OCl_4,8NH_3,3H_2O$. It is evident that the fuscocobaltic salts are ammoniacal compounds of basic cobaltic salts. The normal cobaltic sulphate ought to have the composition $Co_2(SO_4)_3 = Co_2O_3,3SO_3$; the simplest basic salts will be $Co_2O(SO_4)_2 = Co_2O_3,2SO_3$, and $Co_2O_2(SO_4) = Co_2O_3,SO_3$. The fuscocobaltic salts correspond with the first type of basic salts. They are changed (in concentrated solutions) into oxycobaltamine salts by absorption of one atom of oxygen, tion, and in general the relation of nickel, it is important to observe that cobalt more easily forms a higher degree of oxidation—namely,

$Co_2O_3(SO_4)_3$. The whole process of oxidation will be as follows: first of all Co_2X_4, a cobaltous salt, is in the solution (X a univalent haloid, 2 molecules of the salt being taken), then Co_2OX_4, the basic cobaltic salt (4th series), then $Co_2O_2X_4$, the salt of the dioxide (2nd series). The series of basic salts with an acid, 2HX, forms water and a normal salt, Co_2X_6 (in 3, 5, 6 series). These salts are combined with various amounts of water and ammonia. Under many conditions the salts of fuscocobalt are easily transformed into salts of the next series. The salts of the series that has just been described contain 4 molecules of ammonia to 1 atom of cobalt.

(*e*) *The roseocobaltic* (or roseopentamine), $CoX_3H_2O,5NH_3$, *salts*, like the luteocobaltic, correspond with the normal cobaltic salts, but contain less ammonia, and an extra molecule of water. Thus the sulphate is obtained from cobaltous sulphate dissolved in ammonia and left exposed to the air until transformed into a brown solution of the fuscocobaltic salt; when this is treated with sulphuric acid a crystalline powder of the roseocobaltic salt, $Co_2(SO_4)_3,10NH_3,5H_2O$, separates. The formation of this salt is easily understood: cobaltous sulphate in the presence of ammonia absorbs oxygen, and the solution of the fuscocobaltic salt will therefore contain, like cobaltous sulphate, one part of sulphuric acid to every part of cobalt, so that the whole process of formation may be expressed by the equation: $10NH_3 + 2CoSO_4 + H_2SO_4 + 4H_2O + O$ $Co_2(SO_4)_3,10NH_3,5H_2O$. This salt forms tetragonal crystals of a red colour, slightly soluble in cold, but readily soluble in warm water. When the sulphate is treated with baryta, roseocobaltic hydroxide is formed in the solution, which absorbs the carbonic anhydride of the air. It is obtained from the next series by the action of alkalis.

(*f*) The *roseotetramine cobaltic salts* $CoCl_3,2H_2O,4NH_3$ were obtained by Jörgensen, and belong to the type of the luteo-salts, only with the substitution of $2NH_3$ for H_2O. Like the luteo- and roseo-salts they give double salts with $PtCl_4$, similar to the alkaline double salts, for instance $(Co2H_2O,4NH_3)2(SO_4)_2Cl_2PtCl_4$. They are darker in colour than the preceding, but also crystallise well. They are formed by dissolving $CoCO_3$ in sulphuric acid (of a given strength), and after NH_3 and carbonate of ammonium have been added, air is passed through the solution (for oxidation) until the latter turns red. It is then evaporated with lumps of carbonate of ammonium, filtered from the precipitate and crystallised. A salt of the composition $Co_2(CO_3)_2(SO_4),(2H_2O,4NH_3)_2$ is thus obtained, from which the other salts may be easily prepared.

(*g*) The *purpureocobaltic salts*, $CoX_3,5NH_3$, are also products of the direct oxidation of ammoniacal solutions of cobalt salts. They are easily obtained by heating the roseocobaltic and luteo-salts with strong acids. They are to all effects the same as the roseocobaltic salts, only anhydrous. Thus, for instance, the purpureocobaltic chloride, $Co_2Cl_6,10NH_3$, or $CoCl_3,5NH_3$, is obtained by boiling the oxycobaltamine salts with ammonia. There is the same distinction between these salts and the preceding ones as between the various compounds of cobaltous chloride with water. In the purpureocobaltic only X_2 out of the X_3 react (are ionised). To the roseotetramine salts (*f*) there correspond the *purpureotetramine* salts, $CoX_3H_2O,4NH_3$. The corresponding chromium purpureopentamine salt, $CrCl_3,5NH_3$ is obtained with particular ease (Christensen, 1898). Dry anhydrous chromium chloride is treated with anhydrous liquid ammonia in a freezing mixture composed of liquid CO_2 and chlorine, and after some time the mixture is taken out of the freezing mixture, so that the excess of NH_3 boils away; the violet crystals then immediately acquire the red colour of the salt, $CrCl_3,5NH_3$, which is formed. The product is washed with water (to extract the luteo-salt, $CrCl_3,6NH_3$), which does not dissolve the salt, and it is then recrystallised from a hot solution of hydrochloric acid.

(*h*) The *praseocobaltic salts*, $CoX_3,4NH_3$, are green, and form, with respect to the roseotetramine salts (*f*), the products of ultimate dehydration (for example, like metaphosphoric acid with respect to orthophosphoric acid, but in dissolving in water they give neither roseotetramine nor tetramine salts. (In my opinion one should expect salts with a still smaller amount of NH_3, of the blue colour proper to the low hydrated compounds *sesquioxide of cobalt, cobaltic oxide*, Co_2O_3—than nickel, especially in the presence of hypochlorous acid. If a solution of a cobalt salt be

of cobalt; the green colour of the praseo-salts already forms a step towards the blue.) Jörgenson obtained salts for ethylene-diamine, $N_2H_4C_2H_4$ which replaces $2NH_3$. After being kept a long time in aqueous solution they give roseotetramine salts, just as metaphosphoric acid gives orthophosphoric acid, while the roseotetramine salts are converted into praseo-salts by Ag_2O and NaHO. Here only one X is ionised out of the X_3. There are also basic salts of the same type; but the best known is the chromium salt called the rhodozochromic salt, $Cr_2(OH)_3Cl_3,6NH_3,2H_2O$, which is formed by the prolonged action of water upon the corresponding roseo-salt.

The cobaltamine compounds differ essentially but little from the ammoniacal compounds of other metals. The only difference is that here the cobaltic oxide is obtained from the cobaltous oxide in the presence of ammonia. In any case it is a simpler question than that of the double cyanides. Those forces in virtue of which such a considerable number of ammonia molecules are united with a molecule of a cobalt compound, appertain naturally to the series of those slightly investigated forces which exist even in the highest degrees of combination of the majority of elements. They are the same forces which lead to the formation of compounds containing water of crystallisation, double salts, isomorphous mixtures and complex acids (Chapter XXI., Note 8 bis). The simplest conception, according to my opinion, of cobalt compounds (much more so than by assuming special complex radicles, with Schiff, Weltsien, Claus, and others), may be formed by comparing them with other ammoniacal products. Ammonia, like water, combines in various proportions with a multitude of molecules. Silver chloride and calcium chloride, just like cobalt chloride, absorb ammonia, forming compounds which are sometimes slightly stable, and easily dissociated, sometimes more stable, in exactly the same way as water combines with certain substances, forming fairly stable compounds called hydroxides or hydrates, or less stable compounds which are called compounds with water of crystallisation. Naturally the difference in the properties in both cases depends on the properties of those elements which enter into the composition of the given substances, and on those kinds of affinity towards which chemists have not as yet turned their attention. If boron fluoride, silicon fluoride, &c., combine with hydrofluoric acid, if platinic chloride, and even cadmium chloride, combine with hydrochloric acid, these compounds may be regarded as double salts, because acids are salts of hydrogen. But evidently water and ammonia have the same saline faculty, more especially as they, like haloid acids, contain hydrogen, and are both capable of further combination—for instance, ammonia with hydrochloric acid. Hence it is simpler to compare complex ammoniacal with double salts, hydrates, and similar compounds, but *the ammonio-metallic salts* present a most complete qualitative and quantitative resemblance to *the hydrated salts of metals*. The composition of the latter is $MX_n mH_2O$, where M = metal, X = the haloid, simple or complex, and *n* and *m* the quantities of the haloid and so-called water of crystallisation respectively. The composition of the ammoniacal salts of metals is $MX_n mNH_3$. The water of crystallisation is held by the salt with more or less stability, and some salts even do not retain it at all; some part with water easily when exposed to the air, others when heated, and then with difficulty. In the case of some metals all the salts combine with water, whilst with others only a few, and the water so combined may then be easily disengaged. All this applies equally well to the ammoniacal salts, and therefore the combination of ammonia may be termed *the ammonia of crystallisation*. Just as the water which is combined with a salt is held by it with different degrees of force, so it is with ammonia. In combining with $2NH_3$, $PtCl_2$ evolves 31,000 cals.; while $CaCl_2$ only evolves 14,000 cals.; and the former compound parts with its NH_3 (together with HCl in this case) with more difficulty, only above 200°, while the latter disengages ammonia at 180°. $ZnCl_2,2NH_3$ in forming $ZnCl_2,4NH_3$ evolves only 11,000 cals., and splits up again into its components at 80°. The amount of combined ammonia is as variable as the amount of water of crystallisation—for instance, $SnI_4 8NH_3$, $CrCl_2 8NH_3$, $CrCl_3 6NH_3$, $CrCl_3 5NH_3$, $PtCl_2 4NH_3$, &c. are known. Very often NH_3 is replaceable by OH_2 and conversely.

mixed with barium carbonate and an excess of hypochlorous acid be added, or chlorine gas be passed through it, then at the ordinary

colourless, anhydrous cupric salt—for instance, cupric sulphate—when combined with water forms blue and green salts, and violet when combined with ammonia. If steam be passed through anhydrous copper sulphate the salt absorbs water and becomes heated; if ammonia be substituted for the water the heating becomes much more intense, and the salt breaks up into a fine violet powder. With water $CuSO_4,5H_2O$ is formed, and with ammonia $CuSO_4,5NH_3$, the number of water and ammonia molecules retained by the salt being the same in each case, and as a proof of this, and that it is not an isolated coincidence, the remarkable fact must be borne in mind that water and ammonia consecutively, molecule for molecule, are capable of supplanting each other, and forming the compounds $CuSO_4,5H_2O$, $CuSO_4,4H_2O,NH_3$; $CuSO_4,3H_2O,2NH_3$; $CuSO_4,2H_2O,3NH_3$; $CuSO_4,H_2O,4NH_3$, and $CuSO_4,5NH_3$. The last of these compounds was obtained by Henry Rose, and my experiments have shown that more ammonia than this cannot be retained. By adding to a strong solution of cupric sulphate sufficient ammonia to dissolve the whole of the oxide precipitated, and then adding alcohol, Berzelius obtained the compound $CuSO_4,H_2O,4NH_3$, &c. The law of substitution also assists in rendering these phenomena clearer, because a compound of ammonia with water forms ammonium hydroxide, NH_4HO, and therefore these molecules combining with one another may also interchange, as being of equal value. In general, those salts form stable ammoniacal compounds which are capable of forming stable compounds with water of crystallisation; and as ammonia is capable of combining with acids, and as some of the salts formed by slightly energetic bases in their properties more closely resemble acids (that is, salts of hydrogen) than those salts containing more energetic bases, we might expect to find more stable and more easily-formed ammonio-metallic salts with metals and their oxides having weaker basic properties than with those which form energetic bases. This explains why the salts of potassium, barium, &c., do not form ammonio-metallic salts, whilst the salts of silver, copper, zinc, &c., easily form them, and the salts RX_3 still more easily and with greater stability. This consideration also accounts for the great stability of the ammoniacal compounds of cupric oxide compared with those of silver oxide, since the former is displaced by the latter. It also enables us to see clearly the distinction which exists in the stability of the cobaltamine salts containing salts corresponding with cobaltous oxide, and those corresponding with higher oxides of cobalt, for the latter are weaker bases than cobaltous oxides. *The nature of the forces and quality of the phenomena occurring during the formation of the most stable substances, and of such compounds as crystallisable compounds, are one and the same, although perhaps exhibited in a different degree.* This, in my opinion, may be best confirmed by examining the compounds of carbon, because for this element the nature of the forces acting during the formation of its compounds is well known. Let us take as an example two unstable compounds of carbon. Acetic acid, $C_2H_4O_2$ (specific gravity 1·06), with water forms the hydrate, $C_2H_4O_2,H_2O$, denser (1·07) than either of the components, but unstable and easily decomposed, generally simply referred to as a solution. Such also is the crystalline compound of oxalic acid, $C_2H_2O_4$, with water, $C_2H_2O_4,2H_2O$. Their formation might be predicted as starting from the hydrocarbon C_2H_6, in which, as in any other, the hydrogen may be exchanged for chlorine, the water residue (hydroxyl), &c. The first substitution product with hydroxyl, $C_2H_5(HO)$, is stable; it can be distilled without alteration, resists a temperature higher than 100°, and then does not give off water. This is ordinary alcohol. The second, $C_2H_4(HO)_2$, can also be distilled without change, but can be decomposed into water and C_2H_4O (ethylene oxide or aldehyde); it boils at about 197°, whilst the first hydrate boils at 78°, a difference of about 100°. The compound $C_2H_3(HO)_3$ will be the third product of such substitution; it ought to boil at about 300°, but does not resist this temperature—it decomposes into H_2O and $C_2H_4O_2$, where only one hydroxyl group remains, and the other atom of oxygen is left in the same condition as in ethylene oxide, C_2H_4O. There is a proof of this. Glycol, $C_2H_4(HO)_2$, boils at 197°, and forms water and ethylene oxide, which temperature on shaking, the whole of the cobalt will be separated in the form of black cobaltic oxide : $2CoSO_4 + ClHO + 2BaCO_3$

boils at 18° (aldehyde, its isomeride, boils at 21°); therefore the product disengaged by the splitting up of the hydrate boils at 184° lower than the hydrate $C_2H_4(HO)_2$. Thus the hydrate $C_2H_3(HO)_3$, which ought to boil at about 300°, splits up in exactly the same way into water and the product $C_2H_4O_2$, which boils at 117°—that is, nearly 183° lower than the hydrate, $C_2H_3(HO)_3$. But this hydrate splits up before distillation. The above-mentioned hydrate of acetic acid is such a decomposable hydrate—that is to say, what is called a solution. Still less stability may be expected from the following hydrates. $C_2H_2(HO)_4$ also splits up into water and a hydrate (it contains two hydroxyl groups) called glycollic acid, $C_2H_2O(HO)_2 = C_2H_4O_3$. The next product of substitution will be $C_2H(HO)_5$; it splits up into water, H_2O, and glyoxylic acid, $C_2H_4O_4$ (three hydroxyl groups). The last hydrate which ought to be obtained from C_2H_6, and ought to contain $C_2(HO)_6$, is the crystalline compound of oxalic acid, $C_2H_2O_4$ (two hydroxyl groups), and water, $2H_2O$, which has been already mentioned. The hydrate $C_2(HO)_6 = C_2H_2O_4,2H_2O$, ought, according to the foregoing reasoning, to boil at about 600° (because the hydrate, $C_2H_4(HO)_2$, boils at about 200°, and the substitution of 4 hydroxyl groups for 4 atoms of hydrogen will raise the boiling-point 400°). It does not resist this temperature, but at a much lower point splits up into water, $2H_2O$, and the hydrate $C_2O_2(HO)_2$, which is also capable of yielding water. Without going into further discussion of this subject, it may be observed that the formation of the hydrates, or compounds with water of crystallisation, of acetic and oxalic acids has thus received an accurate explanation, illustrating the point we desired to prove in affirming that compounds with water of crystallisation are held together by the same forces as those which act in the formation of other complex substances, and that the easy displacement of the water of crystallisation is only a peculiarity of a local character, and not a radical point of distinction. All the above-mentioned hydrates, C_2X_6, or products of their destruction, are actually obtained by the oxidation of the first hydrate, $C_2H_5(HO)$, or common alcohol, by nitric acid (Sokoloff and others). Hence the forces which induce salts to combine with nH_2O or with NH_3 are undoubtedly of the same order as the forces which govern the formation of ordinary 'atomic' and saline compounds. (A great impediment in the study of the former was caused by the conviction which reigned in the sixties and seventies, that 'atomic' were essentially different from 'molecular' compounds like crystallohydrates, in which it was assumed that there was a combination of entire molecules, as though without the participation of the atomic forces.) If the bond between chlorine and different metals is not equally strong, so also the bond uniting nH_2O and nNH_3 is exceeding variable; there is nothing very surprising in this. And in the fact that the combination of different amounts of NH_3 and H_2O alters the capacity of the haloids X of the salts RX_3 for reaction (for instance, in the luteo-salts all the X_3, while in the purpureo, only 2 out of the 3, and in the praseo-salts only 1 of the 3 X's reacts), we should see in the first place a phenomenon similar to what we met with in Cr_2Cl_6 (Chapter XXI., Note 7 bis), for in both instances the cause of the difference lies in the removal of water; a molecule $RCl_3,6H_2O$ or $RCl_3,6NH_3$ contains the halogen in a perfectly mobile (ionised) state, while in the molecule $RCl_3,5H_2O$ or $RCl_3,5NH_3$ a portion of the halogen has almost lost its faculty for reaction with $AgNO_3$, just as metalepsical chlorine has lost this faculty which is fully developed in the chloranhydride. Until the reason of this difference be clear, we cannot expect that ordinary points of view and generalisation can give a clear answer. However, we may assume that here the explanation lies in the nature and kind of motion of the atoms in the molecules, although as yet it is not clear how. Nevertheless, I think it well to call attention again (Chapter I.) to the fact that the combination of water, and hence, also of any other element, leads to most diverse consequences; the water in the gelatinous hydrate of alumina or in the decahydrated Glauber salt is very mobile, and easily reacts like water in a free state; but the same water combined with oxide of calcium, or C_2H_4 (for instance, in C_2H_6O and in $C_4H_{10}O$), or with P_2O_5, has become quite different, and

$= Co_2O_3 + 2BaSO_4 + HCl + 2CO_2$. Under those circumstances nickelous oxide does not immediately form black sesquioxide, but after a considerable space of time it also separates in the form of sesquioxide, Ni_2O_3, but always later than cobalt. This is due to the relative difficulty of further oxidation of the nickelous oxide. It is, however, possible to oxidise it; if, for instance, the hydroxide NiH_2O_2 be shaken in water and chlorine gas be passed through it, then nickel chloride will be formed, which is soluble in water, and insoluble nickelic oxide in the form of a black precipitate: $3NiH_2O_2 + Cl_2 = NiCl_2 + Ni_2O_3,3H_2O$. Nickelic oxide may also be obtained by adding sodium hypochlorite mixed with alkali to a solution of a nickel salt. Nickelic and cobaltic hydrates are black. Nickelic oxide evolves oxygen with all acids, and in consequence of this it is not separated as a precipitate in the presence of acids; thus it evolves chlorine with hydrochloric acid, exactly like manganese dioxide. When nickelic oxide is dissolved in aqueous ammonia it liberates nitrogen, and an ammoniacal solution of nickelous oxide is formed. When heated, nickelic oxide loses oxygen, forming

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longer acts like water in a free state. We see the same phenomenon in many other cases—for example, the chlorine in chlorates no longer gives a precipitate of chloride of silver with $AgNO_3$. Thus, although the instance which is found in the difference between the roseo- and purpureo-salts deserves to be fully studied on account of its simplicity, still it is far from being exceptional, and we cannot expect it to be thoroughly explained unless a mass of similar instances, which are exceedingly common among chemical compounds, be conjointly explained. (Among the researches which add to our knowledge respecting the complex ammoniacal compounds, I think it indispensable to call the reader's attention to Prof. Kournakoff's dissertation 'On complex metallic bases,' 1898.)

Kournakoff (1894) showed that the solubility of the luteo-salt, $CoCl_3,6NH_3$, at 0° = 4·80 (per 100 of water), at 20° = 7·7, that in passing into the roseo-salt, $CoCl_3H_2O5NH_3$, the solubility rises considerably, and at 0° = 16·4, and at 20° = about 27, whilst the passage into the purpureo-salt, $CoCl_3,5NH_3$, is accompanied by a great fall in the solubility, namely, at 0° = 0·28, and at 20° = about 0·5. And as crystallohydrates with a smaller amount of water are usually more soluble than the higher crystallohydrates (Le Chatelier), whilst here we find that the solubility falls (in the purpureo-salt) with a loss of water, that water which is contained in the roseo-salt cannot be compared with the water of crystallisation. Kournakoff, therefore, connects the fall in solubility (in the passage of the roseo- into the purpureo-salts) with the accompanying loss in the reactive capacity of the chlorine.

In conclusion, it may be observed that the elements of the eighth group—that is, the analogues of iron and platinum—according to my opinion, will yield most fruitful results when studied as to combinations with whole molecules, as already shown by the examples of complex ammoniacal, cyanogen, nitro-, and other compounds, which are easily formed in this eighth group, and are remarkable for their stability. This faculty of the elements of the eighth group for forming the complex compounds alluded to, is in all probability connected with the position which the eighth group occupies with regard to the others. Following the seventh, which forms the type RX_7, it might be expected to contain the most complex type, RX_8. This is met with in OsO_4. The other elements of the eighth group, however, only form the lower types RX_2, RX_3, RX_4 . . . . and these accordingly should be expected to aggregate themselves into the higher types, which is accomplished in the formation of the above-mentioned complex compounds.

in acetic acid without the evolution of oxygen.[35 bis] But ordinary acids, especially on heating, evolve oxygen, forming a solution of a cobaltous salt. The presence of a cobaltic salt in a solution of a cobaltous salt may be detected by the brown colour of the solution and the black precipitate formed by the addition of alkali, and also from the fact that such solutions evolve chlorine when heated with hydrochloric acid. Cobaltic oxide may not only be prepared by the above-mentioned methods, but also by heating cobalt nitrate, after which a steel-coloured mass remains which retains traces of nitric acid, but when heated further to incandescence evolves oxygen, leaving a compound of cobaltic and cobaltous oxides, similar to magnetic ironstone. Cobalt (but not nickel) undoubtedly forms besides Co_2O_3 a *dioxide* CoO_2. This is obtained[36] when the cobaltous oxide is oxidised by iodine or peroxide of barium.[37]

[35 bis] Marshall (1891) obtained cobaltic sulphate, $Co_2(SO_4)_3,18H_2O$, by the action of an electric current upon a strong solution of $CoSO_4$.

[36] The action of an alkaline hypochlorite or hypobromite upon a boiling solution of cobaltous salts, according to Schroederer (1889), produces oxides, whose composition varies between Co_3O_5 (Rose's compound) and Co_2O_3, and also between Co_5O_8 and $Co_{12}O_{19}$. If caustic potash and then bromine be added to the liquid, only Co_2O_3 is formed. The action of alkaline hypochlorites or hypo-bromites, or of iodine, upon cobaltic salts, gives a highly-coloured precipitate which has a different colour to the hydrate of the oxide $Co_2(OH)_6$. According to Carnot the precipitate produced by the hypochlorites has a composition $Co_{10}O_{16}$, whilst that given by iodine in the presence of an alkali contains a larger amount of oxygen. Fortmann (1891) reinvestigated the composition of the higher oxygen oxide obtained by iodine in the presence of alkali, and found that the greenish precipitate (which disengages oxygen when heated to 100°) corresponds to the formula CoO_2. The reaction must be expressed by the equation: $CoX_2 + I_2 + 4KHO = CoO_2 + 2KX + 2KI + 2H_2O$.

[37] Prior to Fortmann, Rousseau (1889) endeavoured to solve the question as to whether CoO_2 was able to combine with bases. He succeeded in obtaining a barium compound corresponding to this oxide. Fifteen grams of $BaCl_2$ or $BaBr_2$ are triturated with 5–6 grams of oxide of barium, and the mixture heated to redness in a closed platinum crucible; 1 gram of oxide of cobalt is then gradually added to the fused mass. Each addition of oxide is accompanied by a violent disengagement of oxygen. After a short time, however, the mass fuses quietly, and a salt settles at the bottom of the crucible, which, when freed from the residue, appears as black hexagonal, very brilliant crystals. In dissolving in water this substance evolves chlorine; its composition corresponds to the formula $2(CoO_2)BaO$. If the original mass be heated for a long time (40 hours), the amount of dioxide in the resultant mass decreases. The author obtained a neutral salt having the composition CoO_2,BaO (this compound $= BaO_2,CoO$) by breaking up the mass as it agglomerates together, and bringing the pieces into contact with the more heated surface of the crucible. This salt is formed between the somewhat narrow limits of temperature 1,000°–1,100°; above and below these limits compounds richer or poorer in CoO_2 are formed. The formation of CoO_2 by the action of BaO_2, and the easy decomposition of CoO_2 with the evolution of oxygen, give reason for thinking that it belongs to the class of peroxides (like Cr_2O_7, CaO_2, &c.); it is not yet known whether they give peroxide of hydrogen like the true peroxides. The fact that

Nickel alloys possess qualities which render them valuable for technical purposes, the alloy of nickel with iron being particularly remarkable. This alloy is met with in nature as *meteoric iron.* The Pallasoffsky mass of meteoric iron, preserved in the St. Petersburg Academy, fell in Siberia in the last century; it weighs about 15 cwt. and contains 88 p.c. of iron and about 10 p.c. of nickel, with a small admixture of other metals. In the arts *German silver* is most extensively used; it is an alloy containing nickel, copper, and zinc in various proportions. It generally consists of about 50 parts of copper, 25 parts of zinc, and 25 parts of nickel. This alloy is characterised by its white colour resembling that of silver, and, like this latter metal, it does not rust, and therefore furnishes an excellent substitute for silver in the majority of cases where it is used. Alloys which contain silver in addition to nickel show the properties of silver to a still greater extent. Alloys of nickel are used for currency, and if rich deposits of nickel are discovered a wide field of application lies before it, not only in a pure state (because it is a beautiful metal and does not rust) but also for use in alloys. Steel vessels (pressed or forged out of sheet steel) covered with nickel have such practical merits that their manufacture, which has not long commenced, will most probably be rapidly developed, whilst nickel steel, which exceeds ordinary steel in its tenacity, has already proved its excellent qualities for many purposes (for instance, for armour plate).

Until 1890 no compound of cobalt or nickel was known of sufficient volatility to determine the molecular weights of the compounds of these metals; but in 1890 Mr. L. Mond, in conducting (together with Langer and Quincke) his researches on the action of nickel upon carbonic oxide (Chapter IX., Note 24 bis), observed that nickel gradually volatilises in a stream of carbonic oxide; this only takes place at low temperatures, and is seen by the coloration of the flame of the carbonic oxide. This observation led to the discovery of a remarkable volatile *compound of nickel and carbonic oxide*, having as molecular composition $Ni(CO)_4$,[38]

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it is obtained by means of iodine (probably through HIO), and its great resemblance to MnO_2 leads rather to the supposition that CoO_2 is a very feeble saline oxide. The form CoO_2 is repeated in the cobaltic compounds (Note 86), and the existence of CoO_2 should have long ago been recognised upon this basis.

[38] This compound is known as nickel tetra-carbonyl. It appears to me yet premature to judge of the structure of such an extraordinary compound as $Ni(CO)_4$. It has long been known that potassium combines with CO forming $K_n(CO)_n$ (Chapter IX., Note 81), but this substance is apparently saline and non-volatile, and has as little in common with $Ni(CO)_4$ as Na_2H has with SbH_3. However, Berthelot observed that when NiC_4O_4 is kept in air, it oxidises and gives a colourless compound, $Ni_3C_2O_3,10H_2O$, having apparently saline properties. We may add that Schutzenberger, on reducing $NiCl_2$ by heating it in a current of hydrogen, observed that a nickel compound partially volatilises with the HCl and gives metallic nickel when heated again. The platinum compound,

as determined by the vapour density and depression of the freezing point. Cobalt and many other metals do not form volatile compounds under these conditions, but iron gives a similar product (Note 26 bis). $Ni(CO)_4$ is prepared by taking finely divided Ni (obtained by reducing NiO by heating it in a stream of hydrogen, or by igniting the oxalate NiC_2O_4)[39] and passing (at a temperature below 50°, for even at 60° decomposition may take place and an explosion) a stream of CO over it; the latter carries over the vapour of the compound, which condenses (in a well-cooled receiver) into a perfectly colourless extremely mobile liquid, boiling without decomposition at 43°, and crystallising in needles at −25° (Mond and Nasini, 1891). Liquid $Ni(CO)_4$ has a sp. gr. 1·356 at 0°, is insoluble in water, dissolves in alcohol and benzene, and burns with a very smoky flame due to the liberation of Ni. The vapour when passed through a tube heated to 180° and above deposits a brilliant coating of metal, and disengages CO. If the tube be strongly heated the decomposition is accompanied by an explosion. If $Ni(CO)_4$ as vapour be passed through a solution of $CuCl_2$, it reduces the latter to metal; it has the same action upon an ammoniacal solution of AgCl, strong nitric acid oxidises $Ni(CO)_4$, dilute solutions of acids have no action; if the vapour be passed through strong sulphuric acid, CO is liberated, chlorine gives NiCl and $COCl_2$; no simple reactions of double decomposition are yet known for $Ni(CO)_4$, however, so that its connection with other carbon compounds is not clear. Probably the formation of this compound could be applied for extracting nickel from it ores.[40]

$PtCl_2(CO)_3$ (Chapter XXIII., Note 11), offers the greatest analogy to $Ni(CO)_4$. This compound was obtained as a volatile substance by Schutzenberger by moderately heating (to 285°) metallic platinum in a mixture of chlorine and carbonic oxide. If we designate CO by Y, and an atom of chlorine by X, then taking into account that, according to the periodic system, Ni is an analogue of Pt, a certain degree of correspondence is seen in the composition NiY_4 and PtX_2Y_2. It would be interesting to compare the reactions of the two compounds.

[39] According to its empirical formula oxalate of nickel also contains nickel and carbonic oxide.

[40] The following are the thermo-chemical data (according to Thomsen, and referred to gram weights expressed by the formula, in large calories or thousand units of heat) for the formation of corresponding compounds of Mn, Fe, Co, Ni, and Cu (+Aq signifies that the reaction proceeds in an excess of water):

	R = Mn	Fe	Co	Ni	Cu
$R+Cl_2+Aq$	128	100	95	94	63
$R+Br_2+Aq$	106	78	73	72	41
$R+I_2+Aq$	76	48	43	41	32
$R+O+H_2O$	95	68	63	61	38
$R+O_2+SO_2+nH_2O$	193	169	163	163	130
RCl_2+Aq	+16	18	18	19	11

These examples show that for analogous reactions the amount of heat evolved in passing from Mn to Fe, Co, Ni, and Cu varies in regular sequences as the atomic weight increases. A similar difference is to be found in other groups and series, and proves that thermo-chemical phenomena are subject to the periodic law

CHAPTER XXIII

THE PLATINUM METALS

THE six metals: ruthenium, Ru, rhodium, Rh, palladium, Pd, osmium, Os, iridium, Ir, and platinum, Pt, are met with associated together in nature. Platinum always predominates over the others, and hence they are known as the *platinum metals.* By their chemical character their position in the periodic system is in the eighth group, corresponding with iron, cobalt, and nickel.

The natural transition from titanium and vanadium to copper and zinc by means of the elements of the iron group is demonstrated by all the properties of these elements, and in exactly the same manner a transition from zirconium, niobium, and molybdenum to silver, cadmium, and indium, through ruthenium, rhodium, and palladium, is in perfect accordance with fact and with the magnitude of the atomic weights, as also is the position of osmium, iridium, and platinum between tantalum and tungsten on the one side, and gold and mercury on the other. In all these three cases the elements of smaller atomic weight (chromium, molybdenum, and tungsten) are able, in their higher grades of oxidation, to give acid oxides having the properties of distinct but feebly energetic acids (in the lower oxides they give bases), whilst the elements of greater atomic weight (zinc, cadmium, mercury), even in their higher grades of oxidation, only give bases, although with feebly developed basic properties. The platinum metals present the same intermediate properties such as we have already seen in iron and the elements of the eighth group.

In the platinum metals the intermediate properties *of feebly acid and feebly basic metals* are developed with great clearness, so that there is not one sharply-defined acid anhydride among their oxides, although there is a great diversity in the grades of oxidation from the type RO_4 to R_2O. The feebleness of the chemical forces observed in the platinum metals is connected with the ready decomposability of their compounds, with the small atomic volume of the metals themselves, and with their large atomic weight. The oxides of platinum, iridium, and osmium can scarcely be termed either basic or acid; they are capable of combinations of both kinds, each of which is feeble. They are all intermediate oxides.

The atomic weights of platinum, iridium, and osmium are nearly 191 to 196, and of palladium, rhodium, and ruthenium, 104 to 106. Thus, strictly speaking, we have here two series of metals, which are, moreover, perfectly parallel to each other; three members in the first series, and three members in the second—namely, platinum presents an analogy to palladium, iridium to rhodium, and osmium to ruthenium. As a matter of fact, however, the whole *group* of the platinum metals is characterised by *a number of common properties*, both physical and chemical, and, moreover, there are several points of resemblance between the members of this group and those of the *iron* group (Chapter XXII.) The atomic volumes (Table III., column 18) of the elements of this group are *nearly equal* and *very small*. The iron metals have atomic volumes of nearly 7, whilst that of the metals allied to palladium is nearly 9, and of those adjacent to platinum (Pt, Ir, Os,) nearly 9·4. This comparatively small atomic volume corresponds with the great infusibility and tenacity proper to all the iron and platinum metals, and to their small chemical energy, which stands out very clearly in the heavy platinum metals. All the platinum metals are very *easily reduced* by ignition and by the action of various reducing agents, in which process oxygen, or a haloid group, is disengaged from their compounds and the metal left behind. This is a property of the platinum metals which determines many of their reactions, and the circumstance of their always being found in nature in *a native state*. In Russia in the Urals (discovered in 1819) and in Brazil (1735) platinum is obtained from alluvial deposits, but in 1892 Professor Inostranzeff discovered a vein deposit of platinum in serpentine near Tagil in the Urals.[1] The facility with which they are reduced is so great that their chlorides are even decomposed by gaseous hydrogen, especially when shaken up and heated under a certain pressure. Hence it will be readily understood that such metals as zinc, iron, &c., separate them from solutions with great ease, which fact is taken advantage of in practice and in the chemical treatment of the platinum metals.[1 bis]

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[1] Wells and Penfield (1889) have described a mineral sperrylite (found in the Canadian gold-bearing quartz) and consisting of platinum diarsenide, $PtAs_2$. It is a remarkable fact that this mineral clearly confirms the position of platinum in the same group as iron, because it corresponds in crystalline form (regular octahedron) and chemical composition with iron pyrites, FeS_2.

[1 bis] Some light is thrown upon the facility with which the platinum compounds decompose by Thomsen's data, showing that in an excess of water (+Aq) the formation

All the platinum metals, like those of the iron group, are grey, with a comparatively feeble metallic lustre, and are very infusible. In this respect they stand in the same order as the metals of the iron series; nickel is more fusible and whiter than cobalt and iron, so also palladium is whiter and more fusible than rhodium and ruthenium, and platinum is comparatively more fusible and whiter than iridium or osmium. The saline compounds of these metals are red or yellow, like those of the majority of the metals of the iron series, and like the latter, the different forms of oxidation present different colours. Moreover, certain complex compounds of the platinum metals, like certain complex compounds of the iron series, either have particular characteristic tints or else are colourless.

The platinum metals are found *in nature associated together in alluvial deposits* in a few localities, from which they are washed, owing to their very considerable density, which enables a stream of water to wash away the sand and clay with which they are mixed. Platinum deposits are chiefly known in the Urals, and also in Brazil and a few other localities. The platinum ore washed from these alluvial deposits presents the appearance of more or less coarse grains, and sometimes, as it were, of semi-fused nuggets.[2]

All the platinum metals give compounds with the halogens, and the highest haloid type of combination for all is RX_4. For the majority of the platinum metals this type is exceedingly unstable; the lower compounds corresponding to the type RX_2, which are formed by the separation of X_2, are more stable. In the type RX_2 the platinum metals form more stable salts, which offer no little resemblance to

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from platinum, of such a double salt as $PtCl_4,2KCl$, is accompanied by a comparatively small evolution of heat (*see* Chapter XXI., Note 40), for instance, $Pt + Cl_4 + 2KCl + Aq$ only evolves about 88,000 calories (hence the reaction, $Pt + Cl_4 + Aq$, will evidently disengage still less, because $PtCl_4 + 2KCl$ evolves a certain amount of heat), whilst on the other hand, $Fe + Cl_3 + Aq$ gives 100,000 calories, and even the reaction with copper (for the formation of the double salt) evolves 68,000 calories.

[2] The largest amount of platinum is extracted in the Urals, about five tons annually. A certain amount of gold is extracted from the washed platinum by means of mercury, which does not dissolve the platinum metals but dissolves the gold accompanying the platinum in its ores. Moreover, the ores of platinum always contain metals of the iron series associated with them. The washed and mechanically sorted ore in the majority of cases contains about 70 to 80 p.c. of platinum, about 5 to 8 p.c. of iridium, and a somewhat smaller quantity of osmium. The other platinum metals—palladium, rhodium, and ruthenium—occur in smaller proportions than the three above named. Sometimes grains of almost pure osmium-iridium, containing only a small quantity of other metals, are found in platinum ores. This *osmium-iridium* may be easily separated from the other platinum metals, owing to its being nearly insoluble in aqua regia, by which the latter are easily dissolved. There are grains of platinum which are magnetic. The grains of osmium-iridium are very hard and malleable, and are therefore used for certain purposes, for instance, for the tips of gold pens.

the kindred compounds of the iron series—for example, to nickelous chloride, $NiCl_2$, cobaltous chloride, $CoCl_2$, &c. This even expresses itself in a similarity of volume (platinous chloride, $PtCl_2$, volume, 46; nickelous chloride, $NiCl_2 = 50$), although in the type RX_2 the true iron metals give very stable compounds, whilst the platinum metals frequently react after the manner of suboxides, decomposing into the metal and higher types, $2RX_2 = R + RX_4$. This probably depends on the facility with which RX_2 decomposes into R and X_2, when X_2 combines with the remaining portion of RX_2

As in the series iron, cobalt, nickel, nickel gives NiO and Ni_2O_3, whilst cobalt and iron give higher and varied forms of oxidation, so also among the platinum metals, platinum and palladium only give the forms RX_2 and RX_4, whilst rhodium and iridium form another and intermediate type, RX_3, also met with in cobalt, corresponding with the oxide, having the composition R_2O_3, besides which they form an acid oxide, like ferric acid, which is also known in the form of salts, but is in every respect unstable. *Osmium* and *ruthenium*, like manganese, form still higher oxides, and in this respect exhibit the greatest diversity. They not only give RX_2, RX_3, RX_4, and RX_6, but also a still *higher form of oxidation*, RO_4, which is not met with in any other series. This form is exceedingly characteristic, owing to the fact that the oxides, OsO_4 and RuO_4, are volatile and have feebly acid properties. In this respect they most resemble permanganic anhydride, which is also somewhat volatile.[3]

When dissolved in aqua regia ($PtCl_4$ is formed) and liberated from the solution by sal ammoniac ($(NH_4)_2PtCl_6$ is formed) and reduced by ignition (which may be done by Zn and other reducing agents, direct from a solution of $PtCl_4$) platinum[3 bis] forms a powdery mass, known

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[3] In characterising the platinum metals according to their relations to the iron metals, it is very important to add two more very remarkable points. The platinum metals are capable of forming a sort of unstable compound with hydrogen; they absorb it and only part with it when somewhat strongly heated. This faculty is especially developed in platinum and palladium, and it is very characteristic that nickel, which exactly corresponds with platinum and palladium in the periodic system, should exhibit the same faculty for retaining a considerable quantity of hydrogen (Graham's and Raoult's experiments). Another characteristic property of the platinum metals consists in their easily giving (like cobalt which forms the cobaltic salts) stable and characteristic saline compounds with ammonia, and like Fe and Co, double salts with the cyanides of the alkali metals, especially in their lower forms of combination. All the above so clearly brings the elements of the iron series into close relationship with the platinum metals that the periodic system acquires as natural a character as can be required, with a certain individuality for each element.

[3 bis] Platinum was first obtained in the last century from Brazil, where it was called silver (platinea). Watson in 1750 characterised platinum as a separate independent metal. In 1803 Wollaston discovered palladium and rhodium in crude platinum, and at

as spongy platinum or platinum black. If this powder of platinum be heated and pressed, or hammered in a cylinder, the grains aggregate or forge together, and form a continuous, though of course not entirely homogeneous, mass. Platinum was formerly, and is even now, worked up in this manner. The platinum money formerly used in Russia was made in this way. Sainte-Claire Deville, in the fifties, for the first time melted platinum in considerable quantities by employing a special furnace made in the form of a small reverberatory furnace, and composed of two pieces of lime, on which the heat of the oxyhydrogen flame has no action. Into this furnace (shown in fig. 34, Vol. I. p. 175)—or, more strictly speaking, into the cavity made in the pieces of lime—the platinum is introduced, and two orifices are made in the lime; through one, the upper, or side orifice, is introduced an oxyhydrogen gas burner, in which either detonating gas or a mixture of oxygen and coal-gas is burnt, whilst the other orifice serves for the escape of the products of combustion and certain impurities which are more volatile than the platinum, and especially the oxidised compounds of osmium, ruthenium, and palladium, which are comparatively easily volatilised by heat. In this manner the platinum is converted into a continuous metallic form by means of fusion, and this method is now used for melting considerable masses of platinum[4] and its alloys with iridium.

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about the same time Tennant distinguished iridium and osmium in it. Professor Claus, of Kazan, in his researches on the platinum metals (about 1840) discovered ruthenium in them, and to him are due many important discoveries with regard to these elements, such as the indication of the remarkable analogy between the series Pd—Rh—Ru and Pt—Ir—Os.

The treatment of platinum ore is chiefly carried on for the extraction of the platinum itself and its alloys with iridium, because these metals offer a greater resistance to the action of chemical reagents and high temperatures than any of the other malleable and ductile metals, and therefore the wire so often used in the laboratory and for technical purposes is made from them, as also are various vessels used for chemical purposes in the laboratory and in works. Thus sulphuric acid is distilled in platinum retorts, and many substances are fused, ignited, and evaporated in the laboratory in platinum crucibles and on platinum foil. Gold and many other substances are dissolved in dishes made of iridium-platinum, because the alloys of platinum and iridium are but slightly attacked when subjected to the action of aqua regia.

The comparatively high density (about 21·5), hardness, ductility, and infusibility (it does not melt at a furnace heat, but only in the oxyhydrogen flame or electric furnace), as well as the fact of its resisting the action of water, air, and other reagents, renders an alloy of 90 parts of platinum and 10 parts of iridium (Deville's platinum-iridium alloy) a most valuable material for making standard weights and measures, such as the metre, kilogram, and pound, and therefore all the newest standards of most countries are made of this alloy.

[4] This process has altered the technical treatment of platinum to a considerable extent. It has in particular facilitated the manufacture of alloys of platinum with iridium and rhodium from the pure platinum ores, since it is sufficient to fuse the ore in order for the greater amount of the osmium to burn off, and for the mass to fuse into a homogeneous, malleable alloy, which can be directly made use of. There is very little ruthenium in the ores of platinum. If during fusion lead be added, it dissolves

To obtain pure platinum, the ore is treated with aqua regia in which only the osmium and iridium are insoluble. The solution contains the platinum metals in the form RCl_4, and in the lower forms of chlorination, RCl_3 and RCl_2, because some of these metals—for instance, palladium and rhodium—form such unstable chlorides of the type RX_4 that they partially decompose even when diluted with water, and pass into the stable lower type of combination; in addition to which the chlorine is very easily disengaged if it comes in contact with substances on which it can act. In this respect platinum resists the action of heat and reducing agents better than any of its companions—that is, it passes with greater difficulty from $PtCl_4$ to the lower compound $PtCl_2$. On this is based the method of preparation of more or less pure platinum. Lime or sodium hydroxide is added to the solution in aqua regia until neutralised, or only containing a very slight excess of alkali. It is best to first evaporate and slightly ignite the solution, in order to remove the excess of acid, and by heating it to partially convert the higher chlorides of the palladium, &c., into the lower. The addition of alkalis completes the reduction, because the chlorine held in the compounds RX_4 acts on the alkali like free chlorine, converting it into a hypochlorite. Thus palladium chloride, $PdCl_4$, for example, is converted into palladious chloride, $PdCl_2$, by this means, according to the equation $PdCl_4 + 2NaHO = PdCl_2 + NaCl + NaClO + H_2O$. In a similar manner iridic chloride, $IrCl_4$, is converted into the trichloride, $IrCl_3$, by this method. When this conversion takes place the platinum still remains in the form of platinic chloride, $PtCl_4$. It is then possible to take advantage of a certain difference in the properties of the higher and lower chlorides of the platinum metals. Thus lime precipitates the lower chlorides of the members of the platinum metals occurring in solution without acting on the platinic chloride, $PtCl_4$, and hence the addition of a large proportion of lime immediately precipitates the associated metals, leaving the platinum itself in solution in the form of a soluble double salt, $PtCl_4,CaCl_2$. A far better and more perfect

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the platinum (and other platinum metals) owing to its being able to form a very characteristic alloy containing PtPb. If an alloy of the two metals be left exposed to moist air, the excess of lead is converted into carbonate (white lead) in the presence of the water and carbonic acid of the air, whilst the above platinum alloy remains unchanged. The white lead may be extracted by dilute acid, and the alloy PtPb remains unaltered. The other platinum metals also give similar alloys with lead. The fusibility of these alloys enables the platinum metals to be separated from the gangue of the ore, and they may afterwards be separated from the lead by subjecting the alloy to oxidation in furnaces furnished with a bone ash bed, because the lead is then oxidised and absorbed by the bone ash, leaving the platinum metals untouched. This method of treatment was proposed by H. Sainte-Claire Deville in the sixties, and is also used in the analysis of these metals (*see* further on).

separation is effected *by means of ammonium chloride*, which gives, with platinic chloride, an insoluble yellow precipitate, $PtCl_4,2NH_4Cl$, whilst it forms soluble double salts with the lower chlorides RCl_2 and RCl_3, so that ammonium chloride precipitates the platinum only from the solution obtained by the preceding method. These methods are employed for preparing the platinum which is used for the manufacture of platinum articles, because, having platinum in solution as calcium platinochloride, $PtCaCl_6$, or as the insoluble ammonium platinochloride, $Pt(NH_4)_2Cl_6$, the platinum compound in every case, after drying or ignition, loses all the chlorine from the platinic chloride and leaves finely-divided metallic platinum, which may be converted into homogeneous metal by compression and forging, or by fusion.[5]

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[5] For the ultimate purification of platinum from palladium and iridium the metals must be re-dissolved in aqua regia, and the solution evaporated until the residue begins to evolve chlorine. The residue is then re-precipitated with ammonium or potassium chloride. The precipitate may still contain a certain amount of iridium, which passes with greater difficulty from the tetrachloride, $IrCl_4$, into the trichloride, $IrCl_3$, but it will be quite free from palladium, because the latter easily loses its chlorine and passes into palladious chloride, $PdCl_2$, which gives an easily-soluble salt with potassium chloride. The precipitate, containing a small quantity of iridium, is then heated with sodium carbonate in a crucible, when the mass decomposes, giving metallic platinum and iridium oxide. If potassium chloride has been employed, the residue after ignition is washed with water and treated with aqua regia. The iridium oxide remains undissolved, and the platinum easily passes into solution. Only cold and dilute aqua regia must be used. The solution will then contain pure platinic chloride, which forms the starting-point for the preparation of all platinum compounds. Pure platinum for accurate researches (for instance, for the unit of light, according to Violle's method) may be obtained (Mylius and Foerster, 1892) by Finkener's method, by dissolving the impure metal in aqua regia (it should be evaporated to drive off the nitrogen compounds), and adding NaCl so as to form a double sodium salt, which is purified by crystallising with a small amount of caustic soda, washing the crystals with a strong solution of NaCl, and then dissolving them in a hot 1 p.c. solution of soda, repeating the above and ultimately igniting the double salt, previously dried at 120°, in a stream of hydrogen; platinum black and NaCl are then formed. The three following are very sensitive tests (to thousandths of a per cent.) for the presence of Ir, Ru, Rh, Pd (osmium is not usually present in platinum which has once been purified, since it easily volatilises with Cl_2 and CO_2, and in the first treatment of the crude platinum either passes off as OsO_4 or remains undissolved), Fe, Cu, Ag, and Pb: (1) the assay is alloyed with 10 parts of pure lead, the alloy treated with dilute nitric acid (to remove the greater part of the Pb), and dissolved in aqua regia; the residue will consist of Ir and Ru; the Pb is precipitated from the nitric acid solution by sulphuric acid, whilst the remaining platinum metals are reduced from the evaporated solution by formic acid, and the resultant precipitate fused with $KHSO_4$; the Pd and Rh are thus converted into soluble salts, and the former is then precipitated by HgC_2N_2. (2) Iron may be detected by the usual reagents, if the crude platinum be dissolved in aqua regia, and the platinum metals precipitated from the solution by formic acid. (3) If crude platinum (as foil or sponge) be heated in a mixture of chlorine and carbonic oxide it volatilises (with a certain amount of Ir, Pd, Fe, &c.) as $PtCl_2,2CO$ (Note 11), whilst the whole of the Rh, Ag, and Cu it may contain remains behind. Among other characteristic reactions for the platinum metals, we may mention: (1) that rhodium is precipitated from the solution obtained after fusion with $KHSO_4$ (in which Pt does not dissolve) by NH_3, acetic and formic acids; (2) that dilute aqua regia dissolves precipitated Pt, but not Rh; (3) that

Metallic *platinum* in a fused state has a specific gravity of 21; it is grey; softer than iron but harder than copper, exceedingly ductile, and therefore easily drawn into wire and rolled into thin sheets, and may be hammered into crucibles and drawn into thin tubes, &c. In the state in which it is obtained by the ignition of its compounds, it forms a spongy mass, known as spongy platinum, or else as powder (platinum black).[6] In either case it is dull grey, and is characterised, as we already know, by the faculty of absorbing hydrogen and other gases. Platinum is not acted on by hydrochloric, hydriodic, nitric, and sulphuric acids, or a mixture of hydrofluoric and nitric acids. Aqua regia, and any liquid containing chlorine or able to evolve chlorine or bromine, dissolves platinum. Alkalis are decomposed by platinum at a red heat, owing to the faculty of the platinum oxide, PtO_2, formed to combine with alkaline bases, inasmuch as it has a feebly-developed acid character (*see* Note 8). Sulphur, phosphorus (the phosphide, PtP_2,

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if the insoluble residue of the platinum metals (Ir, Ru, Os) obtained, after treating with aqua regia, be fused with a mixture of 1 part of KNO_3 and 3 parts of K_2CO_3 (in a gold crucible), and then treated with water, it gives a solution containing the Ru (and a portion of the Ir), but which throws it all down when saturated with chlorine and boiled; (4) that if iridium be fused with a mixture of KHO and KNO_3, it gives a soluble potassium salt, IrK_2O_4 (the solution is blue), which, when saturated with chlorine, gives $IrCl_4$, which is precipitated by NH_4Cl (the precipitate is black), forming a double salt, leaving metallic Ir after ignition; (5) that rhodium mixed with NaCl and ignited in a current of chlorine gives a soluble double salt (from which sal-ammoniac separates Pt and Ir), which gives (according to Jörgensen) a difficultly soluble purpureo-salt (Chapter XXII., Note 35), $Rh_2Cl_6,5NH_3$, when treated with NH_3; in this form the Rh may be easily purified and obtained in a metallic form by igniting in hydrogen; and (6) that palladium, dissolved in aqua regia and dried (NH_4Cl throws down any Pt), gives soluble $PdCl_2$, which forms an easily crystallisable yellow salt, $PdCl_2NH_3$, with ammonia; this salt (Wilm) may be easily purified by crystallisation, and gives metallic Pd when ignited. These reactions illustrate the method of separating the platinum metals from each other.

[6] We have already become acquainted with the effect of finely-divided platinum on many gaseous substances. It is best seen in the so-called *platinum black*, which is a coal-black powder left by the action of sulphuric acid on the alloy of zinc and platinum, or which is precipitated by metallic zinc from a dilute solution of platinum. In any case, finely-divided platinum absorbs gases more powerfully and rapidly the more finely divided and porous it is. Sulphurous anhydride, hydrogen, alcohol, and many organic substances in the presence of such platinum are easily oxidised by the oxygen of the air, although they do not combine with it directly. The absorption of oxygen is as much as several hundred volumes per one volume of platinum, and the oxidising power of such absorbed oxygen is taken advantage of not only in the laboratory but even in manufacturing processes. Asbestos or charcoal, soaked in a solution of platinic chloride and ignited, is very useful for this purpose, because by this means it becomes coated with platinum black. If 50 grams of $PtCl_4$ be dissolved in 60 c.c. of water, and 70 c.c. of a strong (40 p.c.) solution of formic aldehyde added, the mixture cooled, and then a solution of 50 grams of NaHO in 50 grams of water added, the platinum is precipitated. After washing with water the precipitate passes into solution and forms a black liquid containing *soluble colloidal platinum* (Loew, 1890). If the precipitated platinum be allowed to absorb oxygen on the filter, the temperature rises 40°, and a very porous *platinum black* is obtained which vigorously facilitates oxidation.

is formed), arsenic and silicon all act more or less rapidly on platinum, under the influence of heat. Many of the metals form alloys with it. Even charcoal combines with platinum when it is ignited with it, and therefore carbonaceous matter cannot be subjected to prolonged and powerful ignition in platinum vessels. Hence a platinum crucible soon becomes dull on the surface in a smoky flame. Platinum also forms alloys with zinc, lead, tin, copper, gold, and silver.[7] Although mercury does not directly dissolve platinum, still it forms a solution or amalgam with spongy platinum in the presence of sodium amalgam; a similar amalgam is also formed by the action of sodium amalgam on a solution of platinum chloride, and is used for physical experiments.

There are *two kinds* of *platinum compounds*, PtX_4 and PtX_2. The former are produced by an excess of halogen in the cold, and the latter by the aid of heat or by the splitting up of the former. The starting-point for the platinum compounds is *platinum tetrachloride, platinic chloride*, $PtCl_4$, obtained by dissolving platinum in aqua regia.[7 bis] The solution crystallises in the cold, in a desiccator, in the form of reddish-brown deliquescent crystals which contain hydrochloric acid, $PtCl_4,2HCl,6H_2O$, and behave like a true acid whose salts correspond to the formula R_2PtCl_6—ammonium platinochloride, for example.[7 tri] The hydrochloric acid is liberated from these crystals by gently heating or evaporating the solution to dryness; or, better still, after treatment with silver nitrate a reddish-brown mass remains behind, which dissolves in water, and forms a yellowish-red solution which on cooling deposits crystals of the composition $PtCl_4,8H_2O$. The *tendency* of $PtCl_4$ *to combine* with hydrochloric acid and water—that is, *to form higher crystalline compounds*—is evident in the platinum compounds, and must be taken into account in explaining the properties of platinum and the formation of many other of its complex compounds. Dilute solutions of platinic chloride are yellow, and are completely reduced by hydrogen, sulphurous anhydride, and many reducing agents, which first convert the platinic chloride into the lower compound platinous chloride, $PtCl_2$. That faculty which reveals itself in platinum tetrachloride of combining with water of crystallisation and hydrochloric acid is distinctly marked in its property, with which we are already acquainted, of giving precipitates with the salts of potassium, ammonium, rubidium, &c. In general it *readily forms double salts*, $R_2PtCl_6 = PtCl_4 + 2RCl$, where R is a univalent metal such as potassium or NH_4. Hence the addition of a solution of potassium or ammonium chloride to a solution of platinic chloride is followed by the formation of a yellow precipitate, which is sparingly soluble in water and almost entirely insoluble in alcohol and ether (platinic chloride is soluble in alcohol, potassium iridiochloride, IrK_3Cl_6, *i.e.* a compound of $IrCl_3$, is soluble in water but not in alcohol). It is especially remarkable in this case, that the potassium compounds here, as in a number of other instances, separate in an anhydrous form, whilst the sodium compounds, which are soluble in water and alcohol, form red crystals containing water. The composition $Na_2PtCl_6,6H_2O$ exactly corresponds with the above-mentioned hydrochloric compound. The compounds with barium, $BaPtCl_6,4H_2O$, strontium, $SrPtCl_6,8H_2O$, calcium, magnesium, iron, manganese, and many other metals are all soluble in water.[6]

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[7] It is necessary to remark that platinum when alloyed with silver, or as amalgam, is soluble in nitric acid, and in this respect it differs from gold, so that it is possible, by alloying gold with silver, and acting on the alloy with nitric acid, to recognise the presence of platinum in the gold, because nitric acid does not act on gold alloyed with silver.

[7 bis] $PtCl_4$ is also formed by the action of a mixture of HCl vapour and air, and by the action of gaseous chlorine upon platinum.

[7 tri] Pigeon (1891) obtained fine yellow crystals of $PtH_2Cl_6,4H_2O$ by adding strong sulphuric acid to a strong solution of $PtH_2Cl_6,6H_2O$ If crystals of $H_2PtCl_6,6H_2O$ be melted in vacuo (60°) in the presence of anhydrous potash, a red-brown solid hydrate is obtained containing less water and HCl, which parts with the remainder at 200°, leaving anhydrous $PtCl_4$. The latter does not disengage chlorine before 220°, and is perfectly soluble in water.

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[6] Nilson (1877), who investigated the platinochlorides of various metals subsequently to Bonsdorff, Topsöe, Clève, Marignac, and others, found that univalent and bivalent metals—such as hydrogen, potassium, ammonium . . . beryllium, calcium, barium—give compounds of such a composition that there is always twice as much chlorine in the platinic chloride as in the combined metallic chloride; for example, $K_2Cl_2,PtCl_4$; $BeCl_2,PtCl_4,8H_2O$, &c. Such trivalent metals as aluminium, iron (ferric), chromium, didymium, cerium (cerous) form compounds of the type RCl_3PtCl_4, in which the amounts of chlorine are in the ratio 3 : 4. Only indium and yttrium give salts of a different composition—namely, $2InCl_3,5PtCl_4,36H_2O$ and $4YCl_3,5PtCl_4,51H_2O$. Such quadrivalent metals as thorium, tin, zirconium give compounds of the type $RCl_4,PtCl_4$, in which the ratio of the chlorine is 1 : 1. In this manner the valency of a metal may, to a certain extent, be judged from the composition of the double salts formed with platinic chloride.

Platinic bromide, $PtBr_4$, and iodide, PtI_4, are analogous to the tetrachloride, but the iodide is decomposed still more easily than the chloride. If sulphuric acid be added to platinic chloride, and the solution evaporated, it forms a black porous mass like charcoal, which deliquesces in the air, and has the composition $Pt(SO_4)_2$. But this, the only oxygen salt of the type PtX_4, is exceedingly unstable. This is due to the fact that *platinum oxide*, the oxide of the type PtO_2, has a feeble acid character. This is shown in a number of instances. Thus if a strong solution of platinic chloride treated with sodium carbonate be exposed to the action of light or evaporated to dryness and then washed with water, a sodium platinate, $Pt_3Na_2O_7,6H_2O$, remains. The composition of this salt, if we regard it in the same sense as we did the salts of silicic, titanic, molybdic and other acids, will be $PtO(ONa)_2,2PtO_2,6H_2O$—that is, the same type is repeated as we saw in the crystalline compounds of platinum tetrachloride with sodium chloride, or with hydrochloric acid—namely, the type $PtX_4 8Y$, where Y is the molecule H_2O,HCl, &c. Similar compounds are also obtained with other alkalis. *They will be platinates of the alkalis* in which the platinic oxide, PtO_2, plays the part of an acid oxide. Rousseau (1889) obtained different grades of combination $BaOPtO_2$, $3(BaO)2PtO_2$, &c., by igniting a mixture of $PtCl_4$ and caustic baryta. If such an alkaline compound of platinum be

Platinous chloride, $PtCl_2$, is formed when hydrogen platinochloride, PtH_2Cl_6, is ignited at 300°, or when potassium is heated at 230° in a stream of chlorine. The undecomposed tetrachloride is extracted from the residue by washing it with water, and a greenish-grey or brown insoluble mass of the dichloride (sp. gr. 5·9) is then obtained. It is soluble in hydrochloric acid, giving an acid solution of the composition $PtCl_2,2HCl$, corresponding with the type of double salts PtR_2Cl_4. Although platinous chloride decomposes below 500°, still it is formed to a small extent at higher temperatures. Troost and Hautefeuille, and Seelheim observed that when platinum was strongly ignited in a stream of chlorine, the metal, as it were, slowly volatilised and was deposited in crystals; a volatile chloride, probably platinous chloride, was evidently formed in this case, and decomposed subsequently to its formation, depositing crystals of platinum.

The properties of platinum above-described are repeated more or less distinctly, or sometimes with certain modifications, in the above-mentioned associates and analogues of this metal. Thus although palladium forms $PdCl_4$, this form passes into $PdCl_2$ with extreme ease.[9] Whilst

treated with acetic acid, the alkali combines with the latter, and a *platinic hydroxide*, $Pt(OH)_4$, remains as a brown mass, which loses water and oxygen when ignited, and in so doing decomposes with a slight explosion. When slightly ignited this hydroxide first loses water and gives the very unstable oxide PtO_2. Platinic sulphide, PtS_2, belongs to the same type; it is precipitated by the action of sulphuretted hydrogen on a solution of platinum tetrachloride. The moist precipitate is capable of attracting oxygen, and is then converted into the sulphate above mentioned, which is soluble in water. This absorption of oxygen and conversion into sulphate is another illustration of the basic nature of PtO_2, so that it clearly exhibits both basic and acid properties. The latter appear, for instance, in the fact that platinic sulphide, PtS_2, gives crystalline compounds with the alkali sulphides.

[9] In comparing the characteristics of the platinum metals, it must be observed that palladium in its form of combination PdX_2 gives saline compounds of considerable stability. Amongst them *palladous chloride* is formed by the direct action of chlorine or aqua regia (not in excess or in dilute solutions) on palladium. It forms a brown solution, which gives a black insoluble precipitate of *palladous iodide*, PdI_2, with solutions of iodides (in this respect, as in many others, palladium resembles mercury in the mercuric compounds HgX_2). With a solution of mercuric cyanide it gives a yellowish white precipitate, palladous cyanide, PdC_2N_2, which is soluble in potassium cyanide, and gives other double salts, $M_2PdC_4N_4$.

That portion of the platinum ore which dissolves in aqua regia and is precipitated by ammonium or potassium chloride does not contain palladium. It remains in solution, because the palladic chloride, $PdCl_4$, is decomposed and the palladous chloride formed is not precipitated by ammonium chloride; the same holds good for all the other lower chlorides of the platinum metals. Zinc (and iron) separates out all the unprecipitated platinum metals (and also copper, &c.) from the solution. The palladium is found in these platinum residues precipitated by zinc. If this mixture of metals be treated with aqua regia, all the palladium will pass into solution as palladous chloride with some platinic chloride. By this treatment the main portion of the iridium, rhodium, &c. remains almost undissolved, the platinum is separated from the mixture of palladous and platinic chlorides by a solution of ammonium chloride, and the solution of palladium rhodium and iridium in dissolving in aqua regia also form $RhCl_4$ and

is precipitated by potassium iodide or mercuric cyanide. Wilm (1881) showed that palladium may be separated from an impure solution by saturating it with ammonia; all the iron present is thus precipitated, and, after filtering, the addition of hydrochloric acid to the filtrate gives a yellow precipitate of an ammonio-palladium compound, $PdCl_2,2NH_3$, whilst nearly all the other metals remain in solution. *Metallic palladium* is obtained by igniting the ammonio-compound or the cyanide, PdC_2N_2. It occurs native, although rarely, and is a metal of a whiter colour than platinum, sp. gr. 11·4, melts at about 1,500°; it is much more volatile than platinum, partially oxidises on the surface when heated (Wilm obtained spongy palladium by igniting $PdCl_2,2NH_3$, and observed that it gives PdO when ignited in oxygen, and that on further ignition this oxide forms a mixture of Pd_2O and Pd), and loses its absorbed oxygen on a further rise of temperature. It does not blacken or tarnish (does not absorb sulphur) in the air at the ordinary temperature, and is therefore better suited than silver for astronomical and other instruments in which fine divisions have to be engraved on a white metal, in order that the fine lines should be clearly visible. The most remarkable property of palladium, discovered by Graham, consists in its capacity for *absorbing* a large amount of *hydrogen*. Ignited palladium absorbs as much as 940 volumes of hydrogen, or about 0·7 p.c. of its own weight, which closely approaches to the formation of the compound Pd_3H_2, and probably indicates the formation of *palladium hydride*, Pd_2H. This absorption also takes place at the ordinary temperature—for example, when palladium serves as an electrode at which hydrogen is evolved. In absorbing the hydrogen, the palladium does not change in appearance, and retains all its metallic properties, only its volume increases by about 10 p.c.—that is, the hydrogen pushes out and separates the atoms of the palladium from each other, and is itself compressed to $\frac{1}{900}$ of its volume. This compression indicates a great force of chemical attraction, and is accompanied by the evolution of heat (Chapter II., Note 38). The absorption of 1 grm. of hydrogen by metallic palladium (Favre) is accompanied by the evolution of 4·2 thousand calories (for Pt 20, for Na 13, for K 10 thousand units of heat). Troost showed that the dissociation pressure of palladium hydride is inconsiderable at the ordinary temperature, but reaches the atmospheric pressure at about 140°. This subject was subsequently investigated by A. A. Cracow of St. Petersburg (1894), who showed that at first the absorption of hydrogen by the palladium proceeds like solution, according to the law of Dalton and Henry, but that towards the end it proceeds like a dissociation phenomenon in definite compounds; this forms another link between the phenomenon of solution and of the formation of definite atomic compounds. Cracow's observations for a temperature 18°, showed that the electro-conductivity and tension vary until a compound Pd_2H is reached, and namely, that the tension p rises with the volume v of hydrogen absorbed, according to the law of Dalton and Henry—for instance, for

$p = 2·1$	3·2	5·5	7·7 mm.
$v = 14$	20	34	47

The maximum tension at 18° is 9 mm. At a temperature of about 140° (in the vapour of xylene) the maximum tension is about 760 mm., and when $v = 10 - 50$ vols. the tension (according to Cracow's experiments) stands at 90—450 mm.—that is, increases in proportion to the volume of hydrogen absorbed. But from the point of view of chemical mechanics it is especially important to remark that Moutier clearly showed, through palladium hydride, the similarity of the phenomena which proceed in evaporation and dissociation, which fact Henri Sainte-Claire Deville placed as a fundamental proposition in the theory of dissociation. It is possible upon the basis of the second law of the theory of heat, according to the law of the variation of the tension p of evaporation with the temperature T (counted from −273°), to calculate the latent heat of evaporation L (*see* works on physics) because $424\ L = T\ (1/d - 1/D)\ dp/dt$, where d and D are the weights of cubic measures of the gas (vapour) and liquid. (Thus, for instance, for water, when $t = 100°$, $T = 373$, $d = 0·605$, $D = 960$, $dp/dt = 0·027$ m., $13,596 = 367$, $L = 536$,

$IrCl_4$, but they pass into $RhCl_3$ and $IrCl_3$ [9 bis] very easily when heated

whence 424 L=237,264, and the second portion of the equation 226,144, which is sufficiently near, within the limits of experimental error, *see* Chapter I., Note 11.) The same equation is applicable to the dissociation of Na_2H and K_2H—(Chapter XII., Note 42)—but it has only been verified in this respect for Pd_2H, since Moutier, by calculating the amount of heat L evolved, for $t=20$, according to the variation of the tension (dp/dt) obtained 4·1 thousand calories, which is very near the figure obtained experimentally by Favre (*see* Chapter XII., Note 44). The absorbed hydrogen is easily disengaged by ignition or decreased pressure. The resultant compound does not decompose at the ordinary temperature, but when exposed to air the metal sometimes glows spontaneously, owing to the hydrogen burning at the expense of the atmospheric oxygen. The hydrogen absorbed by palladium acts towards many solutions as a reducing agent; in a word, everything here points to the formation of a definite compound and at the same time of a physically-compressed gas, and forms one of the best examples of the bond existing between chemical and physical processes, to which we have many times drawn attention. It must be again remembered that the other metals of the eighth group, even copper, are, like palladium and platinum, able to combine with hydrogen. The permeability of iron and platinum tubes to hydrogen is naturally due to the formation of similar compounds, but palladium is the most permeable.

[9 bis] *Rhodium* is generally separated, together with iridium, from the residues left after the treatment of native platinum, because the palladium is entirely separated from them, and the ruthenium is present in them in very small traces, whilst the osmium at any rate is easily separated, as we shall soon see. The mixture of rhodium and iridium which is left undissolved in dilute aqua regia is dissolved in chlorine water, or by the action of chlorine on a mixture of the metals with sodium chloride. In either case both metals pass into solution. They may be separated by many methods. In either case (if the action be aided by heat) the rhodium is obtained in the form of the chloride $RhCl_3$, and the iridium as iridious chloride, $IrCl_3$. They both form double salts with sodium chloride which are soluble in water, but the iridium salt is also partially soluble in alcohol, whilst the rhodium salt is not. A mixture of the chlorides, when treated with dilute aqua regia, gives iridic chloride, $IrCl_4$, whilst the rhodium chloride, $RhCl_3$, remains unaltered; ammonium chloride then precipitates the iridium as ammonium iridiochloride, $Ir(NH_4)_2Cl_6$, and on evaporating the rose-coloured filtrate the rhodium gives a crystalline salt, $Rh(NH_4)_3Cl_6$. Rhodium and its various oxides are dissolved when fused with potassium hydrogen sulphate, and give a soluble double sulphate (whilst iridium remains unacted on); this fact is very characteristic for this metal, which offers in its properties many points of resemblance with the iron metals. When fused with potassium hydroxide and chlorate it is oxidised like iridium, but it is not afterwards soluble in water, in which respect it differs from ruthenium. This is taken advantage of for separating rhodium, ruthenium, and iridium. In any case, rhodium under ordinary conditions always gives salts of the type RX_3, and not of any other type; and not only halogen salts, but also oxygen salts, are known in this type, which is rare among the platinum metals. Rhodium chloride, $RhCl_3$, is known in an insoluble anhydrous and also in a soluble form (like CrX_3 or salts of chromic oxide), in which it easily gives double salts, compounds with water of crystallisation, and forms rose-coloured solutions. In this form rhodium easily gives double salts of the two types RhM_3Cl_6 and RhM_2Cl_5—for example, $K_3RhCl_6,3H_2O$ and K_2RhCl_5,H_2O. Solutions of the salts (at least, the ammonium salt) of the first kind give salts of the second kind when they are boiled. If a strong solution of potash be added to a red solution of rhodium chloride and boiled, a black precipitate of the hydroxide $Rh(OH)_3$ is formed; but if the solution of potash is added little by little, it gives a yellow precipitate containing more water. This yellow hydrate of rhodium oxide gives a yellow solution when it is dissolved in acids, which only becomes rose-coloured after being boiled. It is obvious a change here takes place, like the transmutations of the salts of chromic oxide. It is also a remarkable fact that

or when acted upon by substances capable of taking up chlorine (even alkalis, which form bleaching salts). Among the platinum metals, ruthenium and osmium have the most acid character, and although they give $RuCl_4$ and $OsCl_4$ they are easily oxidised to RuO_4 and OsO_4 by the action of chlorine in the presence of water; the latter are volatile and may be distilled with the water and hydrochloric acid, from a solution containing other platinum metals.[9 tri] Thus with respect to

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the black hydroxide, like many other oxidised compounds of the platinoid metals, does not dissolve in the ordinary oxygen acids, whilst the yellow hydroxide is easily soluble and gives yellow solutions, which deposit imperfectly crystallised salts. Metallic rhodium is easily obtained by igniting its oxygen and other compounds in hydrogen, or by precipitation with zinc. It resembles platinum, and has a sp. gr. of 12·1. At the ordinary temperature it decomposes formic acid into hydrogen and carbonic anhydride, with development of heat (Deville). With the alkali sulphites, the salts of rhodium and iridium of the type RX_3 give sparingly-soluble precipitates of double sulphites of the composition $R(SO_3Na)_3,H_2O$, by means of which these metals may be separated from solution, and also may be separated from each other, for a mixture of these salts when treated with strong sulphuric acid gives a soluble iridium sulphate and leaves a red insoluble double salt of rhodium and sodium. It may be remarked that the oxides Ir_2O_3 and Rh_2O_3 are comparatively stable and are easily formed, and that they also form different double salts (for instance, $IrCl_3,3KCl3H_2O$, $RhCl_3,2NH_4Cl\frac{1}{2}H_2O$, $RhCl_3,3NH_4Cl1\frac{1}{2}H_2O$) and compounds like the cobaltia compounds (for instance, luteo-salts $RhX_3,6NH_3$, roseo-salts, $RhX_3H_2O5NH_3$, and purpureo-salts $IrX_3,5NH_3$. &c.) *Iridious oxide*, Ir_2O_3, is obtained by fusing iridious chloride and its compounds with sodium carbonate, and treating the mass with water. The oxide is then left as a black powder, which, when strongly heated, is decomposed into iridium and oxygen; it is easily reduced, and is insoluble in acids, which indicates the feeble basic character of this oxide, in many respects resembling such oxides as cobaltic oxide, ceric or lead dioxide, &c. It does not dissolve when fused with potassium hydrogen sulphate. Rhodium oxide, Rh_2O_3, is a far more energetic base. It dissolves when fused with potassium hydrogen sulphate.

From what has been said respecting the separation of platinum and rhodium it will be understood how the compounds of *iridium*, which is the main associate of platinum, are obtained. In describing the treatment of osmiridium we shall again have an opportunity of learning the method of extraction of the compounds of this metal, which has in recent times found a technical application in the form of its oxide, Ir_2O_3; this is obtained from many of the compounds of iridium by ignition with water, is easily reduced by hydrogen, and is insoluble in acids. It is used in painting on china, for giving a black colour. Iridium itself is more difficultly fusible than platinum, and when fused it does not decompose acids or even aqua regia; it is extremely hard, and is not malleable; its sp. gr. is 22·4. In the form of powder it dissolves in aqua regia, and is even partially oxidised when heated in air, sets fire to hydrogen, and, in a word, closely resembles platinum. Heated in an excess of chlorine it gives iridic chloride, $IrCl_4$, but this loses chlorine at 50°; it is, however, more stable in the form of double salts, which have a characteristic *black* colour—for instance, $Ir(NH_4)_2Cl_6$—but they give iridious chloride, $IrCl_3$, when treated with sulphuric acid.

[9 tri] We have yet to become acquainted with the two remaining associates of platinum—ruthenium and osmium—whose most important property is that they are oxidised even when heated in air, and that they are able to give *volatile* oxides of the form RuO_4 and OsO_4; these have a powerful odour (like iodine and nitrous anhydride). Both these higher oxides are solids; they volatilise with great ease at 100°; the former is yellow

the types of combination, all the platinum metals, under certain circumstances, give compounds of the type RX_4—for instance, RO_2, RCl_4, &c.

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give crystalline salts with bases, and their alkaline solutions partially deposit them again when boiled (an excess of water decomposes the salts). The formulæ OsO_4 and RuO_4 correspond with the vapour density of these oxides. Thus Deville found the vapour density of osmic anhydride to be 128 (by the formula 127·5) referred to hydrogen. Tennant and Vauquelin discovered this compound, and Berzelius, Wöhler, Fritzsche, Struvé, Deville, Claus, Joly, and others helped in its investigation; nevertheless there are still many questions concerning it which remain unsolved. It should be observed that RO_4 is the highest known form for an oxygen compound, and RH_4 is the highest known form for a compound of hydrogen; whilst the highest forms of acid hydrates contain SiH_4O_4, PH_3O_4, SH_2O_4, $ClHO_4$—all with four atoms of oxygen, and therefore in this number there is apparently the limit for the simple forms of combination of hydrogen and oxygen. In combination with *several* atoms of an element, or several elements, there may be more than O_4 or H_4, but a molecule never contains more than four atoms of either O or H to one atom of another element. Thus the simplest forms of combination of hydrogen and oxygen are exhausted by the list RH_4, RH_3, RH_2, RH, RO, RO_2, RO_3, RO_4. The extreme members are RH_4 and RO_4, and are only met with for such elements as carbon, silicon, osmium, ruthenium, which also give RCl_4 with chlorine. In these extreme forms, RH_4 and RO_4, the compounds are the least stable (compare SiH_4, PH_3, SH_2, ClH, or RuO_4, MoO_3, ZrO_2, SrO), and easily give up part, or even all, their oxygen or hydrogen.

The primary source from which the compounds of ruthenium and osmium are obtained is either *osmiridium* (the osmium predominates, from IrOs to $IrOs_4$, sp. gr. from 16 to 21), which occurs in platinum ores (it is distinguished from the grains of platinum by its crystalline structure, hardness, and insolubility in aqua regia), or else those insoluble residues which are obtained, as we saw above, after treating platinum with aqua regia. Osmium predominates in these materials, which sometimes contain from 30 p.c. to 40 p.c. of it, and rarely more than 4 p.c. to 5 p.c. of ruthenium. The process for their treatment is as follows: they are first fused with 6 parts of zinc, and the zinc is then extracted with dilute hydrochloric acid. The osmiridium thus treated is, according to Fritzsche and Struvé's method, then added to a fused mixture of potassium hydroxide and chlorate in an iron crucible; the mass as it begins to evolve oxygen acts on the metal, and the reaction afterwards proceeds spontaneously. The dark product is treated with water, and gives a solution of osmium and ruthenium in the form of soluble salts, R_2OsO_4 and R_2RuO_4, whilst the insoluble residue contains a mixture of oxides of iridium (and some osmium, rhodium, and ruthenium), and grains of metallic iridium still unacted on. According to Frémy's method the lumps of osmiridium are straightway heated to whiteness in a porcelain tube in a stream of air or oxygen, when the very volatile osmic anhydride is obtained directly, and is collected in a well-cooled receiver, whilst the ruthenium gives a crystalline sublimate of the dioxide, RuO_2, which is, however, very difficultly volatile (it volatilises together with osmic anhydride), and therefore remains in the cooler portions of the tube; this method does not give volatile ruthenic anhydride, and the iridium and other metals are not oxidised or give non-volatile products. This method is simple, and at once gives dry, pure osmic anhydride in the receiver, and ruthenium dioxide in the sublimate. The air which passes through the tube should be previously passed through sulphuric acid, not only in order to dry it, but also to remove the organic and reducing dust. The vapour of osmic anhydride must be powerfully cooled, and ultimately passed over caustic potash. A third mode of treatment, which is most frequently employed, was proposed by Wöhler, and consists in slightly heating (in order that the sodium chloride should not melt) an intimate mixture of osmiridium and common salt in a stream of moist chlorine. The metals then form compounds with chlorine and sodium chloride, whilst the osmium

But this is the highest form for only platinum and palladium. The remaining platinum metals further, *like iron, give acids* of the type

give ruthenic anhydride, but is always extracted as the soluble ruthenium salt, K_2RuO_4, obtained by fusion with potassium hydroxide and chlorate or nitrate. When the orange-coloured ruthenate, K_2RuO_4, is mixed with acids, the liberated ruthenic acid immediately decomposes into the volatile ruthenic anhydride and the insoluble ruthenic oxide: $2K_2RuO_4 + 4HNO_3 = RuO_4 + RuO_2,2H_2O + 4KNO_3$. When once one of the above compounds of ruthenium or osmium is procured it is easy to obtain all the remaining compounds, and by reduction (by metals, hydrogen, formic acid, &c.) the metals themselves.

Osmic anhydride, OsO_4, is very easily deoxidised by many methods. It blackens organic substances, owing to reduction, and is therefore used in investigating vegetable and animal, and especially nerve, preparations under the microscope. Although osmic anhydride may be distilled in hydrogen, still complete reduction is accomplished when a mixture of hydrogen and osmic anhydride is slightly ignited (just before it inflames). If osmium be placed in the flame it is oxidised, and gives vapours of osmic anhydride, which become reduced, and the flame gives a brilliant light. Osmic anhydride deflagrates like nitre on red-hot charcoal; zinc, and even mercury and silver, reduce osmic anhydride from its aqueous solutions into the lower oxides or metal; such reducing agents as hydrogen sulphide, ferrous sulphate, or sulphurous anhydride, alcohol, &c., act in the same manner with great ease.

The lower oxides of osmium, ruthenium, and of the other elements of the platinum series are not volatile, and it is noteworthy that the other elements behave differently. On comparing SO_2, SO_3; As_2O_3, As_2O_5; P_2O_3, P_2O_5; CO, CO_2, &c., we observe a converse phenomenon; the higher oxides are less volatile than the lower. In the case of osmium all the oxides, with the exception of the highest, are non-volatile, and it may therefore be thought that this higher form is more simply constituted than the lower. It is possible that osmic oxide, OsO_2, stands in the same relation to the anhydride as C_2H_4 to CH_4—*i.e.* the lower oxide is perhaps Os_2O_4, or is still more polymerised, which would explain why the lower oxides, having a greater molecular weight, are less volatile than the higher oxides, just as we saw in the case of the nitrogen oxides, N_2O and NO.

Ruthenium and osmium, obtained by the ignition or reduction of their compounds in the form of powder, have a density considerably less than in the fused form, and differ in this condition in their capacity for reaction; they are much more difficultly fused than platinum and iridium, although ruthenium is more fusible than osmium. Ruthenium in powder has a specific gravity of 8·5, the fused metal of 12·2; osmium in powder has a specific gravity of 20·0, and when semi fused—or, more strictly speaking, agglomerated—in the oxy-hydrogen flame, of 21·4, and fused 22·5. The powder of slightly heated osmium oxidises very easily in the air, and when ignited burns like tinder, directly forming the odoriferous osmic anhydride (hence its name, from the Greek word signifying odour); ruthenium also oxidises when heated in air, but with more difficulty, forming the oxide RuO_2. The oxides of the types RO, R_2O_3, and RO_2 (and their hydrates) obtained by reduction from the higher oxides, and also from the chlorides, are analogous to those given by the other platinum metals, in which respect osmium and ruthenium closely resemble them. We may also remark that ruthenium has been found in the platinum deposits of Borneo in the form of *laurite*, Ru_2S_3, in grey octahedra of sp. gr. 7·0.

For osmium, Moraht and Wischin (1893) obtained free osmic acid, H_2OsO_4, by decomposing K_2OsO_4 with water, and precipitating with alcohol in a current of hydrogen (because in air volatile OsO_4 is formed); with H_2S, osmic acid gives [illegible] at the ordinary temperature.

Debray and Joly showed that ruthenic anhydride, RuO_4, fuses at 25°, boils at 100°, and evolves oxygen when dissolved in potash, forming the salt $KRuO_4$ (not isomorphous with potassium permanganate).

Joly (1891), who studied the ruthenium compounds in greater detail, showed that the

RO_3 or hydrates, $H_2RO_4 = RO_2(HO)_2$ (the type of sulphuric acid); but they, like ferric and manganic acids, are chiefly known in the form of salts of the composition K_2RO_4 or $K_2R_2O_7$ (like the dichromate). These salts are obtained, like the manganates and ferrates, by fusing the oxides, or even the metals themselves, with nitric, or, better still, with potassium peroxide. They are soluble in water, are easily deoxidised and do not yield the acid anhydrides under the action of acids, but break up, either (like the ferrate) forming oxygen and a basic oxide (iridium and rhodium react in this manner, as they do not give higher forms of oxidation), or passing into a lower and higher form of oxidation—that is, reacting like a manganate (or partly like nitrite or phosphite). Osmium and ruthenium react according to the latter form, as they are capable of giving *higher forms of oxidation*, OsO_4 and RuO_4, and therefore their reactions of decomposition may be essentially represented by the equation · $2OsO_3 = OsO_2 + OsO_4$.[10]

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respects. In general, Ru has much in common with Mn. Joly (1889) also showed that if KNO_3 be added to a solution of $RuCl_3$ containing HCl, the solution becomes hot, and a salt, $RuCl_3NO2KCl$, is formed, which enters into double decomposition and is very stable. Moreover, if $RuCl_3$ be treated with an excess of nitric acid, it forms a salt, $RuCl_3NOH_2O$, after being heated (to boiling) and the addition of HCl. The vapour density of RuO_4, determined by Debray and Joly, corresponds to that formula.

[10] Although palladium gives the same types of combination (with chlorine) as platinum, its reduction to RX_2 is incomparably easier than that of platinic chloride, and in the case of iridium it is also very easy. Iridic chloride, $IrCl_4$, acts as an oxidising agent, readily parts with a fourth of its chlorine to a number of substances, readily evolves chlorine when heated, and it is only at low temperatures that chlorine and aqua regia convert iridium into iridic chloride. In disengaging chlorine iridium more often and easily gives the very stable iridious chloride, $IrCl_3$ (perhaps this substance is $Ir_2Cl_6 = IrCl_2,IrCl_4$, insoluble in water, but soluble in potassium chloride, because it forms the double salt K_3IrCl_6), than the dichloride, $IrCl_2$. This compound, corresponding to IrX_2, is very stable, and corresponds with the *basic oxide*, Ir_2O_3, resembling the oxides Fe_2O_3, Co_2O_3. To this form there correspond ammoniacal compounds similar to those given by cobaltic oxide. Although iridium also gives an acid in the form of the salt $K_2Ir_2O_7$, it does not, like iron (and chromium), form the corresponding chloride, $IrCl_6$. In general, in this as in the other elements, it is impossible to predict the chlorine compounds from those of oxygen. Just as there is no chloride SCl_6, but only SCl_2, so also, although IrO_3 exists, $IrCl_6$ is wanting, the only chloride being $IrCl_4$, and this is unstable, like SCl_2, and easily parts with its chlorine. In this respect rhodium is very much like iridium (as platinum is like palladium). For $RhCl_4$ decomposes with extreme ease, whilst rhodium chloride, $RhCl_3$, is very stable, like many of the salts of the type RhX_3, although like the platinum elements these salts are easily reduced to metal by the action of heat and powerful reagents. There is as close a resemblance between osmium and ruthenium. Osmium when submitted to the action of dry chlorine gives osmic chloride, $OsCl_4$, but the latter is converted by water (as is osmium by moist chlorine) into osmic anhydride, although the greater portion is then decomposed into $Os(HO)_4$ and 4HCl, like a chloranhydride of an acid. In general this acid character is more developed in osmium than in platinum and iridium. Having parted with chlorine, osmic chloride, $OsCl_4$, gives the unstable trichloride, $OsCl_3$, and the stable soluble dichloride, $OsCl_2$, which corresponds with platinous chloride in its properties and

Platinum and its analogues, like iron and its analogues, are able to form complex and comparatively stable cyanogen and ammonia compounds, corresponding with the ferrocyanides and the ammoniacal compounds of cobalt, which we have already considered in the preceding chapter.

If platinous chloride, $PtCl_2$ (insoluble in water), be added by degrees to a solution of potassium cyanide, it is completely dissolved (like silver chloride), and on evaporating the solution deposits rhombic prisms of *potassium platinocyanide*, $PtK_2(CN)_4,3H_2O$. This salt, like all those corresponding with it, has a remarkable play of colours, due to the phenomena of dichromism, and even polychromism, natural to all the platinocyanides. Thus it is yellow and reflects a bright blue light. It is easily soluble in water, effloresces in air, then turns red, and at 100° orange, when it loses all its water. The loss of water does not destroy its stability—that is, it still remains unchanged, and its stability is further shown by the fact that it is formed when potassium ferrocyanide, $K_4Fe(CN)_6$, is heated with platinum black. This salt, first obtained by Gmelin, shows a neutral reaction with litmus; it is exceedingly stable under the action of air, like potassium ferrocyanide, which it resembles in many respects. Thus the platinum in it cannot be detected by reagents such as sulphuretted hydrogen; the potassium may be replaced by other metals by the action of their salts, so that it corresponds with a whole series of compounds, $R_2Pt(CN)_4$, and it is stable, although the potassium cyanide and platinous salts, of which it is composed, individually easily undergo change. When treated with oxidising agents it passes, like the ferrocyanide, into a higher form of combination of platinum. If salts of silver be added to its solution, it gives a heavy white precipitate of silver platinocyanide, $PtAg_2(CN)_4$, which when suspended in water and treated with sulphuretted hydrogen, enters into double decomposition with the latter and forms insoluble silver sulphide, Ag_2S, and soluble *hydroplatinocyanic acid*, $H_2Pt(CN)_4$. If potassium platinocyanide be mixed with an equivalent quantity of sulphuric acid, the hydroplatinocyanic acid liberated may be extracted by a mixture of alcohol and ether. The ethereal solution, when evaporated in a desiccator, deposits bright red crystals of the composition $PtH_2(CN)_4,5H_2O$. This acid colours litmus paper, liberates carbonic anhydride from sodium carbonate, and saturates alkalis, so that it presents an analogy to hydroferrocyanic acid.[11]

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[11] This acid character is explained by the influence of the platinum on the hydrogen, and by the attachment of the cyanogen groups. Thus cyanuric acid, $H_3(CN)_3O_3$, is an energetic acid compared with cyanic acid, HCNO. And the formation of a compound

Ammonia, like potassium cyanide, has the faculty of easily reacting with platinum dichloride, forming compounds similar to the platino-

with five molecules of water of crystallisation, ($PtH_2(CN)_4,5H_2O$), confirms the opinion that platinum is able to form compounds of still higher types than that expressed in its saline compounds, and, moreover, the combination of hydroplatinocyanic acid with water does not reach the limit of the compounds which appears in $PtCl_4,2HCl,6H_2O$.

A whole series of *platinocyanides* of the common type $PtR_2(CN)_4nH_2O$ is obtained by means of double decomposition with the potassium or hydrogen or silver salts. For example, the salts of sodium and lithium contain, like the potassium salt, three molecules of water. The sodium salt is soluble in water and alcohol. The ammonium salt has the composition $Pt(NH_4)_2(CN)_4,2H_2O$ and gives crystals which reflect blue and rose-coloured light. This ammonium salt decomposes at 300°, with evolution of water and ammonium cyanide, leaving a greenish *platinum dicyanide*, $Pt(CN)_2$, which is insoluble in water and acid but dissolves in potassium cyanide, hydrocyanic acid, and other cyanides. The same platinous cyanide is obtained by the action of sulphuric acid on the potassium salts in the form of a reddish-brown amorphous precipitate. The most characteristic of the platinocyanides are those of the alkaline earths. The magnesium salt $PtMg(CN)_4,7H_2O$ crystallises in regular prisms, whose side faces are of a metallic green colour and terminal planes dark blue. It shows a carmine-red colour along the main axis, and dark red along the lateral axes; it easily loses water, ($2H_2O$), at 40°, and then turns blue (it then contains $5H_2O$, which is frequently the case with the platinocyanides). Its aqueous solution is colourless, and an alcoholic solution deposits yellow crystals. The remainder of the water is given off at 230°. It is obtained by saturating platinocyanic acid with magnesia, or else by double decomposition between the barium salt and magnesium sulphate. The strontium salt, $SrPt(CN)_4,4H_2O$ crystallises in milk-white plates having a violet and green iridescence. When it effloresces in a desiccator, its surfaces have a violet and metallic green iridescence. A colourless solution of the barium salt $PtBa(CN)_4,4H_2O$ is obtained by saturating a solution of hydroplatinocyanic acid with baryta, or by boiling the insoluble copper platinocyanide in baryta water It crystallises in monoclinic prisms of a yellow colour, with blue and green iridescence; it loses half its water at 100°, and the whole at 150°. The ethyl salt, $Pt(C_2H_5)_2(CN)_4,2H_2O$, is also very characteristic; its crystals are isomorphous with those of the potassium salt, and are obtained by passing hydrochloric acid into an alcoholic solution of hydroplatinocyanic acid. The facility with which they crystallise, the regularity of their forms, and their remarkable play of colours, renders the preparation of the platinocyanides one of the most attractive lessons of the laboratory.

By the action of chlorine or dilute nitric acid, the platinocyanides are converted into salts of the composition $PtM_2(CN)_5$, which corresponds with $Pt(CN)_3,2KCN$—that is, they express the type of a non-existent form of oxidation of platinum, PtX_3 (*i.e.* oxide Pt_2O_3), just as potassium ferricyanide ($FeCy_3,3KCy$) corresponds with ferric oxide, and the ferrocyanide corresponds with the ferrous oxide. The potassium salt of this series contains $PtK_2(CN)_5,3H_2O$, and forms brown regular prisms with a metallic lustre, and is soluble in water but insoluble in alcohol. Alkalis re-convert this compound into the ordinary platinocyanide $K_2Pt(CN)_4$, taking up the excess of cyanogen. It is remarkable that the salts of the type PtM_2Cy_5 contain the same amount of water of crystallisation as those of the type PtM_2Cy_4. Thus the salts of potassium and lithium contain three, and the salt of magnesium seven, molecules of water, like the corresponding salts of the type of platinous oxide. Moreover, neither platinum nor any of its associates gives any cyanogen compound corresponding with the oxide, *i.e.* having the composition PtK_2Cy_6, just as there are no compounds higher than those which correspond to RCy_3nMCy for cobalt or iron. This would appear to indicate the absence of any such cyanides, and indeed for no element are there yet known any poly-cyanides containing more than three ammonia. Owing to the influence of the ammonia, the X_2 in the resultant compound will represent the same character as it has in

$2COCl_2$, as $PtCl_2$ is able to combine with oxychlorides, and forms somewhat stable compounds.

(*D*) The faculty of platinous chloride for forming stable compounds with divers substances shows itself in the formation of the compound $PtCl_2,PCl_3$ by the action of phosphorus pentachloride at 250° on platinum powder (Pd reacts in a similar manner, according to Fink, 1892). The product contains both phosphorus pentachloride and platinum, whilst the presence of $PtCl_2$ is shown in the fact that the action of water produces *chlorplatino-phosphorous acid*, $PtCl_2P(OH)_3$.

(*E*) After the cyanides, the *double salts* of platinum *formed by sulphurous acid* are most distinguished for their stability and characteristic properties. This is all the more instructive, as sulphurous acid is only feebly energetic, and, moreover, in these, as in all its compounds, it exhibits a dual reaction. The salts of sulphurous acid, R_2SO_3, either react as salts of a feeble bibasic acid, where the group SO_3 presents itself as bivalent, and consequently equal to X_2, or else they react after the manner of salts of a monobasic acid containing the same residue, RSO_3, as occurs in the salts of sulphuric acid. In sulphurous acid this residue is combined with hydrogen, $H(SO_3H)$, whilst in sulphuric acid it is united with the aqueous residue (hydroxyl), $OH(SO_3H)$. These two forms of action of the sulphites appear in their reactions with the platinum salts—that is to say, salts of both kinds are formed, and they both correspond with the type PtH_2X_4. The one series of salts contain $PtH_2(SO_3)_2$, and their reactions are due to the bivalent residue of sulphurous acid, which replaces X_2. The others, which have the composition $PtR_2(SO_3H)_4$, contain sulphoxyl. The latter salts will evidently react like acids; they are formed simultaneously with the salts of the first kind, and pass into them. These salts are obtained either by directly dissolving platinous oxide in water containing sulphurous acid, or by passing sulphurous anhydride into a solution of platinous chloride in hydrochloric acid. If a solution of platinous chloride or platinous oxide in sulphurous acid be saturated with sodium carbonate, it forms a white, sparingly soluble precipitate containing $PtNa_2(SO_3Na)_4,7H_2O$. If this precipitate be dissolved in a small quantity of hydrochloric acid and left to evaporate at the ordinary temperature, it deposits a salt of the other type, $PtNa_2(SO_3)_2,H_2O$, in the form of a yellow powder, which is sparingly soluble in water. The potassium salt analogous to the first salt, $PtK_2(SO_3K)_4,2H_2O$, is precipitated by passing sulphurous anhydride into a solution of potassium sulphite in which platinous oxide is suspended. A similar salt is known for ammonium, and with hydrochloric acid it gives a salt of the second kind, $Pt(NH_4)_2(SO_3)_2,H_2O$. If ammonio-chloride of platinum be added to an aqueous solution of sulphurous anhydride, it is first deoxidised, and chlorine is evolved, forming a salt of the type PtX_4; a double decomposition then takes place with the ammonium sulphite, and a salt of the composition $Pt(NH_4)_2Cl_3(SO_3H)$ is formed (in a desiccator). The acid character of this substance is explained by the fact that it contains the elements SO_3H—sulphoxyl, with the hydrogen not yet displaced by a metal. On saturating a solution of this acid with potassium carbonate it gives orange-coloured crystals of a potassium salt of the composition $Pt(NH_4)_2Cl_3(SO_3K)$. Here it is evident that an equivalent of chlorine in $Pt(NH_4)_2Cl_4$ is replaced by the univalent residue of sulphurous acid. Among these salts, that of the composition $Pt(NH_4)_2Cl_2(SO_3H)_2,H_2O$ is very readily formed, and crystallises in well-formed colourless crystals; it is obtained by dissolving ammonium platinochloride, $Pt(NH_4)_2Cl_4$, in an aqueous solution of sulphurous acid. The difficulty with which sulphurous anhydride and platinum are separated from these salts indicates the same basic character in these compounds as is seen in the double cyanides of platinum. In their passage into a complex salt, the metal platinum and the group SO_2 modify their relations (compared with those of PtX_2 or SO_2X_2), just as the chlorine in the salts $KClO$, $KClO_2$, and $KClO_3$, is modified in its relations as compared with hydrochloric acid or ammoniacal salts ; consequently, the ammoniacal compounds produced from PtX_2 will be salts in which X will be replaceable by various other haloids, just as the metal is replaced in the cyanogen salts ; such is the nature of the *platino-ammonium compounds.* PtX_2 forms compounds with $2NH_3$ and with $4NH_3$, and so also PtX_4 gives (not directly from PtX_4 and ammonia, but from the compounds of PtX_2 by the action of chlorine, &c.) similar compounds with $2NH_3$ and with $4NH_3$.[12]

(F') No less characteristic are the *platinonitrites* formed by platinous oxide. They correspond with nitrous acid, whose salts, RNO_2, contain the univalent radicle, NO_2, which is capable of replacing chlorine, and therefore the salts of this kind should form a common type $PtR_2(NO_2)_4$, and such a salt of potassium has actually been obtained by mixing a solution of potassium platinosochloride with a solution of potassium nitrite, when the liquid becomes colourless, especially if it be heated, which indicates the change in the chemical distribution of the elements. As the liquid decolorises it gradually deposits sparingly soluble, colourless prisms of the potassium salt $K_2Pt(NO_2)_4$, which does not contain any water. With silver nitrate a solution of this salt gives a precipitate of silver platinonitrite, $PtAg_2(NO_2)_4$. The silver of this salt may be replaced by other metals by means of double decomposition with metallic chlorides. The sparingly soluble barium salt, when treated with an equivalent quantity of sulphuric acid, gives a soluble acid, which separates, under the receiver of an air-pump, in red crystals; this acid has the composition $PtH_2(NO_2)_4$. To the potassium salt, $K_2Pt(NO_2)_4$, there correspond (Vèzes, 1892) $K_2Pt(NO_2)_4Br_2$ and $K_2Pt(NO_2)_4Cl_2$ and other compounds of the same type K_2PtX_6, where X is partly replaced by Cl or Br and partly by (NO_2), showing a transition towards the type of the double salts like the platino-ammoniacal salts. (The corresponding double sodium nitrite salt of cobalt is soluble in water, while he K,NH_4 and many other salts are insoluble in water, as I was informed by Prof. K. Winkler in 1894).

In all the preceding complex compounds of Pt we see a common type $PtX_2,2MX$ (*i.e.* of double salts corresponding to PtO) or $PtM_2X_4 = Pt(MX_2)_2$, corresponding to $Pt(HO)_2$ with the replacement of O by its equivalent X_2. Two other facts must also be noted. In the first place these X's generally correspond to elements (like chlorine) or groups (like CN, NO_2, SO_3, &c.), which are capable of further combination. In the second place all the compounds of the type PtM_2X_4 are capable of combining with chlorine or similar elements, and thus passing into compounds of the types PtX_3 or PtX_4.

[12] The platinum salt and ammonia, when once combined together, are no longer subject to their ordinary reactions but form compounds which are comparatively very stable. The question at once suggests itself to all who are acquainted with these phenomena, as to what is the relation of the elements contained in these compounds. The first explanation is that these compounds are salts of ammonium in which the hydrogen is partially replaced by platinum. This is the view, with certain shades of difference, held by many respecting the platino-ammonium compounds. They were regarded in this light by Gerhardt, Schiff, Kolbe, Weltzien, and many others. If we suppose the hydrogen in $2NH_4X$ to be replaced by bivalent platinum (as in the salts PtX_2), we shall obtain $\begin{matrix}NH_3\\NH_3\end{matrix}Pt\begin{matrix}X\\X\end{matrix}$—that is, the compound $PtX_2,2NH_3$. The compound with $4NH_3$ will then be represented by a further substitution of the hydrogen in ammonia by ammonium itself—*i.e.* as $NH_2(NH_4X)_2Pt$ or $PtX_2,4NH_3$. A modification of this view is found in that representation of compounds of this kind which is based on atomicity. As platinum in PtX_2 is bivalent, has two affinities, and ammonia, NH_3, is also bivalent, because nitrogen is quinquivalent and is here only combined with H_3, it is evident what bonds should be represented in $PtX_2,2NH_3$ and in $PtX_2,4NH_3$. In the former, $Pt(NH_3Cl)_2$,

If ammonia acts on a boiling solution of platinous chloride in hydrochloric acid, it produces the green *salt of Magnus* (1829),

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platinum, and by the fifth with chlorine. The other compound is $Pt(NH_3{\cdot}NH_3Cl)_2$—that is, the N is united by one affinity with the other N, whilst the remaining bonds are the same as in the first salt. It is evident that this union or chain of ammonias has no obvious limit, and the most essential fault of such a mode of representation is that it does not indicate at all what number of ammonias are capable of being retained by platinum. Moreover, it is hardly possible to admit the bond between nitrogen and platinum in such stable compounds, for these kinds of affinities are, at all events, feeble, and cannot lead to stability, but would rather indicate explosive and easily-decomposed compounds. Moreover, it is not clear why this platinum, which is capable of giving PtX_4, does not act with its remaining affinities when the addition of ammonia to PtX_2 takes place. These, and certain other considerations which indicate the imperfection of this representation of the structure of the platino-ammonium salts, cause many chemists to incline more to the representations of Berzelius, Claus, Gibbs, and others, who suppose that NH_3 is able to combine with substances, to adjoin itself or pair itself with them (this kind of combination is called 'Paarung') without altering the fundamental capacity of a substance for further combinations. Thus, in $PtX_2,2NH_3$, the ammonia is the associate of PtX_2, as is expressed by the formula $N_2H_6PtX_2$. Without enlarging on the exposition of the details of this doctrine, we will only mention that it, like the first, does not render it possible to foresee a limit to the compounds with ammonia; it isolates compounds of this kind into a special and artificial class; does not show the connection between compounds of this and of other kinds, and therefore it essentially only expresses the fact of the combination with ammonia and the modification in its ordinary reactions. For these reasons we do not hold to either of these proposed representations of the ammonio-platinum compounds, but regard them from the point of view cited above with reference to double salts and water of crystallisation—that is, we embrace all these compounds under the representation of compounds of complex types. The type of the compound $PtX_2,2NH_3$ is far more probably the same as that of $PtX_2,2Z$—*i.e.* as PtX_4, or, still more accurately and truly, it is a compound of the same type as $PtX_2,2KX$ or $PtX_2,2H_2O$, &c. Although the platinum first entered into PtK_2X_4 as the type PtX_2, yet its character has changed in the same manner as the character of sulphur changes when from SO_3 the compound $SO_2(OH)_2$ is obtained, or when $KClO_4$, the higher form, is obtained from KCl. For us as yet there is no question as to *what* affinities hold X_2 and what hold $2NH_3$, because this is a question which arises from the supposition of the existence of different affinities in the atoms, which there is no reason for taking as a common phenomenon. It seems to me that it is most important *as a commencement* to render clear the analogy in the formation of various complex compounds, and it is this analogy of the ammonia compounds with those of water of crystallisation and double salts that forms the main object of the primary generalisation. We recognise in platinum, at all events, not only the four affinities expressed in the compound $PtCl_4$, but a much larger number of them, if only the *summation of affinities* is actually possible. Thus, in sulphur we recognise not two but a much greater number of affinities; it is clear that at least six affinities can act. So also among the analogues of platinum: osmic anhydride, OsO_4, $Ni(CO)_4$, PtH_2Cl_6, &c. indicate the existence of at least eight affinities; whilst, in chlorine, judging from the compound $KClO_4 = ClO_3(OK) = ClX_7$, we must recognise at least seven affinities, instead of the one which is accepted. The latter mode of calculating affinities is a tribute to that period of the development of science when only the simplest hydrogen compounds were considered, and when all complex compounds were entirely neglected (they were placed under the class of molecular compounds). This is insufficient for the present state of knowledge, because we find that, in complex compounds as in the most simple, the same constant types or modes of equilibrium are repeated, and the character of certain elements is greatly modified in the passage from the most simple into very complex

$PtCl_2,2NH_3$, insoluble in water and hydrochloric acid. But, judging by its reactions, this salt has twice this formula. Thus, Gros (1837), on boiling Magnus's salt with nitric acid, observed that half the chlorine was replaced by the residue of nitric acid and half the platinum was disengaged: $2PtCl_2(NH_3)_2 + 2HNO_3 = PtCl_2(NO_3)_2(NH_3)_4 + 2PtCl_2$. The Gros's salt thus obtained, $PtCl_2(NO_3)_24NH_3$ (if Magnus's salt

Judging from the most complex platino-ammonium compounds $PtCl_4,4NH_3$, we should admit the possibility of the formation of compounds of the type PtX_4Y_4, where $Y_4 = 4X_2 = 4NH_3$, and this shows that those forces which form such a characteristic series of double platinocyanides $PtK_2(CN)_4,3H_2O$, probably also determine the formation of the higher ammonia derivatives, as is seen on comparing—

$$\begin{array}{llll} PtCl_2 & NH_3 & Cl_2 & 3NH_3 \\ Pt(CN)_2 & KCN & KCN & 3H_2O. \end{array}$$

Moreover, it is obviously much more natural to ascribe the faculty for combination with nY to the whole of the acting elements—that is, to PtX_2 or PtX_4, and not to platinum alone. Naturally such compounds are not produced with any Y. With certain X's there only combine certain Y's. The best known and most frequently-formed compounds of this kind are those with water—that is, compounds with water of crystallisation. Compounds with salts are double salts; also we know that similar compounds are also frequently formed by means of ammonia. Salts of zinc, ZnX_2, copper, CuX_2, silver, AgX, and many others give similar compounds, but these and many other *ammonio-metallic* saline compounds are unstable, and readily part with their combined ammonia, and it is only in the elements of the platinum group and in the group of the analogues of iron, that we observe the faculty to form stable ammonio-metallic compounds. It must be remembered that the metals of the platinum and iron groups are able to form several high grades of oxidation which have an acid character, and consequently in the lower degrees of combination there yet remain affinities capable of retaining other elements, and they probably retain ammonia, and hold it the more stably, because all the properties of the platinum compounds are rather acid than basic—that is, PtX_n recalls rather HX or SnX_n or CX_n than KX, CaX_2, BaX_2, &c., and ammonia naturally will rather combine with an acid than with a basic substance. Further, a dependence, or certain connection of the forms of oxidation with the ammonia compounds, is seen on comparing the following compounds:

$$\begin{array}{ll} PdCl_2,2NH_3,H_2O & PdCl_2,4NH_3,H_2O \\ PtCl_2,2NH_3 & PtCl_4,4NH_3 \\ RhCl_3,5NH_3 & RuCl_2,4NH_3,3H_2O \\ IrCl_3,5NH_3 & OsCl_2,4NH_3,2H_2O \end{array}$$

We know that platinum and palladium give compounds of lower types than iridium and rhodium, whilst ruthenium and osmium give the highest forms of oxidation; this shows itself in this case also. We have purposely cited the same compounds with $4NH_3$ for osmium and ruthenium as we have for platinum and palladium, and it is then seen that Ru and Os are capable of retaining $2H_2O$ and $3H_2O$, besides Cl_2 and NH_3, which the compounds of platinum and palladium are unable to do. The same ideas which were developed in Note 35, Chapter XXII. respecting the cobaltia compounds are perfectly applicable to the present case, *i.e.* to the *platinia* compounds or ammonia compounds of the platinum metals, among which Rh and Ir give compounds which are perfectly analogous to the cobaltia compounds.

Iridium and rhodium, which easily give compounds of the type RX_3, give compounds (Claus) of the type $IrX_3,5NH_3$, of a rose colour, and $RhX_3,5NH_3$, of a yellow colour. Jörgensen, in his researches on these compounds, showed their entire analogy with the belongs to the type PtX_2, then Gros's salt belongs to the type PtX_4), is soluble in water, and the elements of nitric acid, but not the chlorine, contained in it are capable of easily submitting themselves to double saline decomposition. Thus silver nitrate does not enter into double decomposition with the chlorine of Gros's salt. Most instructive was the circumstance that Gros, by acting on his salt with hydrochloric acid, succeeded in substituting the residue of nitric acid in it by chlorine, and the chlorine thus introduced, easily reacted with silver nitrate. Thus it appeared that Gros's salt contained two varieties of chlorine—one which reacts readily, and the other which reacts with difficulty. The composition of Gros's first salt is $PtCl_2(NH_3)_4(NO_3)_2$; it may be converted into $PtCl_2(NH_3)_4(SO_4)$, and in general into $PtCl_2(NH_3)_4X_2$.[13]

The salt of Magnus when boiled with a solution of ammonia gives the salt (of Reiset's first base) $PtCl_2(NH_3)_4$, and this, when treated with bromine, forms the salt $PtCl_2Br_2(NH_3)_4$, which has the same composition and reactions as Gros's salt. To Reiset's salts there corresponds a soluble, colourless, crystalline *hydroxide*, $Pt(OH)_2(NH_3)_4$, having the properties of a powerful and very energetic *alkali*; it attracts carbonic anhydride from the atmosphere, precipitates metallic salts like potash, saturates active acids, even sulphuric, forming colourless (with nitric, carbonic, and hydrochloric acids), or yellow (with sulphuric acid), salts of the type $PtX_2(NH_3)_4$.[14] The comparative stability (for instance, as compared with AgCl and NH_3) of such compounds, and the existence of many other compounds analogous

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[13] Subsequently, a whole series of such compounds was obtained with various elements in the place of the (non-reacting) chlorine, and nevertheless they, like the chlorine, reacted with difficulty, whilst the second portion of the X's introduced into such salts easily underwent reaction. This formed the most important reason for the interest which the study of the composition and structure of the platino-ammonium salts subsequently presented to many chemists, such as Reiset, Blomstrand, Peyrone, Raeffski, Gerhardt, Buckton, Clève, Thomsen, Jörgensen, Kournakoff, Verner, and others. The salts $PtX_4,2NH_3$, discovered by Gerhardt, also exhibited several different properties in the two pairs of X's. In the remaining platino-ammonium salts all the X's appear to react alike.

The quality of the X's, retainable in the platino-ammonium salts, may be considerably modified, and they may frequently be wholly or partially replaced by hydroxyl. For example, the action of ammonia on the nitrate of Gerhardt's base, $Pt(NO_3)_4,2NH_3$, in a boiling solution, gradually produces a yellow crystalline precipitate which is nothing else than a *basic hydrate* or *alkali*, $Pt(OH)_4,2NH_3$. It is sparingly soluble in water, but gives directly soluble salts $PtX_4,2NH_3$ with acids. The stability of this hydroxide is such that potash does not expel ammonia from it, even on boiling, and it does not change below 130°. Similar properties are shown by the hydroxide $Pt(OH)_2,2NH_3$ and the oxide $PtO,2NH_3$ of Reiset's second base. But the hydroxides of the compounds containing $4NH_3$ are particularly remarkable. The presence of ammonia renders them soluble and energetic. The brevity of this work does not permit us, however, to mention many interesting particulars in connection with this subject.

[14] Hydroxides are known corresponding with Gros's salts, which contain one hydroxyl

and those hydroxides do not at once show the properties of alkalis, just as the chlorine which stands in the same place does not react distinctly; but still, after the prolonged action of acids, this hydroxyl group is also replaced by acids. Thus, for example, the action of nitric acid on $Pt(NO_3)_2Cl_2,4NH_3$ causes the non-active chlorine to react, but in the product all the chlorine is not replaced by NO_3, but only half, and the other half is replaced by the hydroxyl group: $Pt(NO_3)_2Cl_2,4NH_3 + HNO_3 + H_2O = Pt(NO_3)_3(OH),4NH_3 + 2HCl$; and this is particularly characteristic, because here the hydroxyl group has not reacted with the acid—an evident sign of the non-alkaline character of this residue. I think it may be well to call attention to the fact that the composition of the ammonio-metallo-salts very often exhibits a correspondence between the amount of X's and the amount of NH_3, of such a nature that we find they contain either XNH_3 or the grouping $X2NH_3$; for example, $Pt(XNH_3)_2$ and $Pt(X2NH_3)_2$, $Co(X2NH_3)_3$, $Pt(XNH_3)_4$, &c. Judging from this, the view of the constitution of the double cyanides of platinum given in Note 11 finds some confirmation here, but, in my opinion, all questions respecting the composition (and structure) of the ammoniacal, double, complex, and crystallisation compounds stand connected with the solution of questions respecting the formation of compounds of various degrees of stability, among which a theory of solutions must be included, and therefore I think that the time has not yet come for a complete generalisation of the data which exist for these compounds; and here I again refer the reader to Prof. Kournakoff's work cited in Chapter XXII., Note 35. However, we may add a few individual remarks concerning the platinia compounds.

To the common properties of the platino-ammonium salts, we must add not only their *stability* (feeble acids and alkalis do not decompose them, the ammonia is not evolved by heating, &c.), but also the fact that the ordinary reactions of platinum are concealed in them to as great an extent as those of iron in the ferricyanides. Thus neither alkalis nor hydrogen sulphide will separate the platinum from them. For example, sulphuretted hydrogen in acting on Gros's salts gives sulphur, removes half the chlorine by means of its hydrogen, and forms salts of Reiset's first base. This may be understood or explained by considering the platinum in the molecule as covered, walled up by the ammonia, or situated in the centre of the molecule, and therefore inaccessible to reagents. On this assumption, however, we should expect to find clearly-expressed ammoniacal properties, and this is not the case. Thus ammonia is easily decomposed by chlorine, whilst in acting on the platino-ammonium salts containing PtX_2 and $2NH_3$ or $4NH_3$, chlorine combines and does not destroy the ammonia; it converts Reiset's salts into those of Gros and Gerhardt. Thus from $PtX_2,2NH_3$ there is formed $PtX_2Cl_2,2NH_3$, and from $PtX_2,4NH_3$ the salt of Gros's base $PtX_2Cl_2,4NH_3$. This shows that the amount of chlorine which combines is not dependent on the amount of ammonia present, but is due to the basic properties of platinum. Owing to this some chemists suppose the ammonia to be inactive or passive in certain compounds. It appears to me that these relations, these modifications, in the usual properties of ammonia and platinum are explained directly by their mutual combination. Sulphur, in sulphurous anhydride, SO_2, and hydrogen sulphide, SH_2, is naturally one and the same, but if we only knew of it in the form of hydrogen sulphide, then, having obtained it in the form of sulphurous anhydride, we should consider its properties as hidden. The oxygen in magnesia, MgO, and in nitric peroxide, NO_2, is so different that there is no resemblance. Arsenic no longer reacts in its compounds with hydrogen as it reacts in its compounds with chlorine, and in their compounds with nitrogen all metals modify both their reactions and their physical properties. We are accustomed to judge the metals by their saline compounds with haloid groups, and ammonia by its compounds with acid substances, and here, in the platino-compounds, if we assume the platinum to be bound to the entire mass of the ammonia—to its hydrogen and nitrogen—we shall understand that both the platinum to them, endows them with a particular chemical interest. Thus Kournakoff (1889) obtained a series of corresponding compounds contain-

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tion of the chlorine (and other haloid simple and complex groups) in Gros's salts acts in a different manner from the other portion, and why only half of it acts in the usual way. But this also is not an exclusive case. The chlorine in potassium chlorate or in carbon tetrachloride does not react with the same ease with metals as the chlorine in the salts corresponding with hydrochloric acid. In this case it is united to oxygen and carbon, whilst in the platino-ammonium compounds it is united partly to platinum and partly to the platino-ammonium group. Many chemists, moreover, suppose that a part of the chlorine is united directly to the platinum and the other part to the nitrogen of the ammonia, and thus explain the difference of the reactions; but chlorine united to platinum reacts as well with a silver salt as the chlorine of ammonium chloride, NH_4Cl, or nitrosyl chloride, $NOCl$, although there is no doubt that in this case there is a union between the chlorine and nitrogen. Hence it is necessary to explain the absence of a facile reactive capacity in a portion of the chlorine by the conjoint influence of the platinum and ammonia on it, whilst the other portion may be admitted as being under the influence of the platinum only, and therefore as reacting as in other salts. By admitting a certain kind of stable union in the platino-ammonium grouping, it is possible to imagine that the chlorine does not react with its customary facility, because access to a portion of the atoms of chlorine in this complex grouping is difficult, and the chlorine union is not the same as we usually meet in the saline compounds of chlorine. These are the grounds on which we, in refuting the now accepted explanations of the reactions and formation of the platino-compounds, pronounce the following opinion as to their structure.

In characterising the platino-ammonium compounds, it is necessary to bear in mind that compounds which already contain PtX_4 do not combine directly with NH_3, and that such compounds as $PtX_4,4NH_3$ only proceed from PtX_2, and therefore it is natural to conclude that those affinities and forces which cause PtX_2 to combine with X_2 also cause it to combine with $2NH_3$. And having the compound $PtX_2,2NH_3$, and supposing that in subsequently combining with Cl_2 it reacts with those affinities which produce the compounds of platinic chloride, $PtCl_4$, with water, potassium chloride, potassium cyanide, hydrochloric acid, and the like, we explain not only the fact of combination, but also many of the reactions occurring in the transition of one kind of platino-ammonium salts into another. Thus by this means we explain the fact that (1) $PtX_2,2NH_3$ combines with $2NH_3$, forming salts of Reiset's first base; (2) and the fact that this compound (represented as follows for distinctness), $PtX_2,2NH_3,2NH_3$, when heated, or even when boiled in solution, again passes into $PtX_2,2NH_3$ (which resembles the easy disengagement of water of crystallisation, &c.); (3) the fact that $PtX_2,2NH_3$ is capable of absorbing, under the action of the same forces, a molecule of chlorine, $PtX_2,2NH_3,Cl_2$, which it then retains with energy, because it is attracted, not only by the platinum, but also by the hydrogen of the ammonia; (4) the fact that this chlorine held in this compound (of Gerhardt) will have a position unusual in salts, which will explain a certain (although very feebly-marked) difficulty of reaction; (5) the fact that this does not exhaust the faculty of platinum for further combination (we need only recall the compound $PtCl_4,2HCl,16H_2O$), and that therefore both $PtX_2,2NH_3,Cl_2$ and $PtX_2,2NH_3,2NH_3$ are still capable of combination, whence the latter, with chlorine, gives $PtX_2,2NH_3,2NH_3,Cl_2$, after the type of PtX_4Y_4 (and perhaps higher); (6) the fact that Gros's compounds thus formed are readily re-converted into the salts of Reiset's first base when acted on by reducing agents; (7) the fact that in Gros's salts, $PtX_2,2NH_3(NH_3X)_2$, the newly-attached chlorine or haloid will react with difficulty with salts of silver, &c., because it is attached both to the platinum and to the ammonia, for both of which it has an attraction; (8) the fact that the faculty for further combination is not even yet exhausted in the type of Gros's salts, and that we actually have a compound of Gros's chlorine salt with platinous chloride and with platinic chloride; the salt $PtSO_4,2NH_3,2NH_3,SO_4$ coming thiocarbamide, CSN_2H_4, in the place of ammonia, $PtCl_2,4CSN_2H_4$, and others corresponding with Reiset's salts. Hydroxylamine, and other substances corresponding with ammonia, also give similar compounds. The common properties and composition of such compounds show their entire analogy to the cobaltia compounds (especially for ruthenium and iridium) and correspond to the fact that both the platinum metals and cobalt occur in the same, eighth, group.

molecules is naturally more developed in the lower forms of combination than in the higher. Hence the salts of Reiset's first base—for example, $PtCl_2,2NH_3,2NH_3$—both combine with water and give precipitates (soluble in water but not in hydrochloric acid) of double salts with many salts of the heavy metals—for example, with lead chloride, cupric chloride, and also with platinic and platinous chlorides (Buckton's salts). The latter compounds will have the composition $PtCl_2,2NH_3,2NH_3,PtCl_2$—that is, the same composition as the salts of Reiset's second base, but it cannot be identical with it. Such an interesting case does actually exist. The first salt, $PtCl_2,4NH_3,PtCl_2$, is green, insoluble in water and in hydrochloric acid, and is known as *Magnus's salt*, and the second, $PtCl_2,2NH_3$, is Reiset's yellow, sparingly soluble (in water). They are polymeric, namely, the first contains twice the number of elements held in the second, and at the same time they easily pass into each other. If ammonia be added to a hot hydrochloric acid solution of platinous chloride, it forms the salt $PtCl_2,4NH_3$, but in the presence of an excess of platinous chloride it gives Magnus's salt. On boiling the latter in ammonia it gives a colourless soluble salt of Reiset's first base, $PtCl_2,4NH_3$, and if this be boiled with water, ammonia is disengaged, and a salt of Reiset's second base, $PtCl_2,2NH_3$, is obtained.

A class of platino-ammonium isomerides (obtained by Millon and Thomsen) are also known. Buckton's salts—for example, the copper salt—were obtained by them from the salts of Reiset's first base, $PtCl_2,4NH_3$, by treatment with a solution of cupric chloride, &c., and therefore, according to our method of expression, Buckton's copper salt will be $PtCl_2,4NH_3,CuCl_2$. This salt is soluble in water, but not in hydrochloric acid. In it the ammonia must be considered as united to the platinum. But if cupric chloride be dissolved in ammonia, and a solution of platinous chloride in ammonium chloride is added to it, a violet precipitate is obtained of the same composition as Buckton's salt, which, however, is insoluble in water, but soluble in hydrochloric acid. In this a portion, if not all, of the ammonia must be regarded as united to the copper, and it must therefore be represented as $CuCl_2,4NH_3,PtCl_2$. This form is identical in composition but different in properties (is isomeric) with the preceding salt (Buckton's). The salt of Magnus is intermediate between them, $PtCl_2,4NH_3,PtCl_2$; it is insoluble in water and hydrochloric acid. These and certain other instances of isomeric compounds in the series of the platino-ammonium salts throw a light on the nature of the compounds in question, just as the study of the isomerides of the carbon compounds has served and still serves as the chief cause of the rapid progress of organic chemistry. In conclusion, we may add that (according to the law of substitution) we must necessarily expect all kinds of intermediate compounds between the platino and analogous ammonia derivatives on the one hand, and the complex compounds of nitrous acid on the other. Perhaps the instance of the reaction of ammonia upon osmic anhydride, OsO_4, observed by Fritsche, Frémy, and others, and more fully studied by Joly (1891), belongs to this class. The latter showed that when ammonia acts upon an alkaline solution of OsO_4 the reaction proceeds according to the equation: $OsO_4 + KHO + NH_3 = OsNKO_3 + 2H_2O$. It might be imagined that in this case the ammonia is oxidised, probably forming the residue of nitrous acid (NO), while the type OsO_4 is deoxidised into OsO_2, and a salt, $OsO(NO)(KO)$, of the type OsX_4 is formed. This salt crystallises well in light yellow octahedra. It corresponds to *osmiamic acid*, $OsO(ON)(HO)$, whose anhydride, $[OsO(NO)]_2$, has the composition $Os_2N_2O_3$, which equals $2Os + N_2O_3$ to the same extent as the above-mentioned compound PtCO equals Pt + CO (*see* Note 11).

CHAPTER XXIV

COPPER, SILVER, AND GOLD

That degree of analogy and difference which exists between iron, cobalt, and nickel repeats itself in the corresponding triad ruthenium, rhodium, and palladium, and also in the heavy platinum metals, osmium, iridium, and platinum. These nine metals form Group VIII. of the elements in the periodic system, being the intermediate group between the even elements of the large periods and the uneven, among which we know zinc, cadmium, and mercury in Group II. Copper, silver, and gold complete[1] this transition, because their properties place them in proximity to nickel, palladium, and platinum on the one hand, and to zinc, cadmium, and mercury on the other. Just as Zn, Cd, and Hg; Fe, Ru, and Os; Co, Rh, and Ir; Ni, Pd, and Pt, resemble each other in many respects, so also do Cu, Ag, and Au. Thus, for example, the atomic weight of copper Cu = 63, and in all its properties it stands between Ni = 59 and Zn = 65. But as the transition from Group VIII. to Group II., where zinc is situated, cannot be otherwise than through Group I., so in copper there are certain properties of the elements of Group I. Thus it gives a suboxide, Cu_2O, and salts, CuX, like the elements of Group I., although at the same time it forms an oxide, CuO, and salts CuX_2, like nickel and zinc. In the case of the oxide, CuO, and the salts, CuX_2, copper is analogous to zinc, judging from the insolubility of the carbonates, phosphates, and similar salts, and by the isomorphism, and other characters.[2] In the cuprous salts there is undoubtedly a great resemblance to the silver salts—thus, for example, silver chloride, AgCl, is characterised by it insolubility and capacity of combining with ammonia, and in this respec cuprous chloride closely resembles it, for it is also insoluble in water and combines with ammonia and dissolves in it, &c. Its composition i also RCl, the same as AgCl, NaCl, KCl, &c., and silver in many compounds resembles, and is even isomorphous with, sodium, so that thi again justifies their being brought together. Silver chloride, cuprous chloride, and sodium chloride crystallise in the regular system Besides which, the specific heats of copper and silver require that they should have the atomic weights ascribed to them. To the oxides Cu_2O and Ag_2O there are corresponding sulphides Ag_2S and Cu_2S. They both occur in nature in crystals of the rhombic system, and, what is most important, copper glance contains an isomorphous mixture of them both, and retains the form of copper glance with various proportions of copper and silver, and therefore has the composition R_2S where R = Cu, Ag.

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[1] The perfectly unique position held by copper, silver, and gold in the periodic system of the elements, and the degree of affinity which is found between them, is all the more remarkable, as nature and practice have long isolated these metals from all others by having employed them—for example, for coinage—and determined their relative [illegible] value in conformity with the order (silver between copper and gold) of their atomic weights, &c.

[2] Cupric sulphate contains 5 molecules of water, $CuSO_4,5H_2O$, and the isomorphous mixtures with $ZnSO_4,7H_2O$ contain either 5 or 7 equivalents, according to whether copper or zinc predominates (Vol. II. p. 6). If there be a large proportion of copper, and if the mixture contain $5H_2O$, the form of the isomorphous mixture (triclinic) will be isomorphous with cupric sulphate, $CuSO_4,5H_2O$, but if a large amount of zinc (or magnesium, iron, nickel, or cobalt) be present the form (rhombic or monoclinic) will be nearly the same

Notwithstanding the resemblance in the atomic composition of the cuprous compounds, CuX, and silver compounds, AgX, with the compounds of the alkali metals KX, NaX, there is a considerable degree of difference between these two series of elements. This difference is clearly seen in the fact that the alkali metals belong to those elements which combine with extreme facility with oxygen, decompose water, and form the most alkaline bases; whilst silver and copper are oxidised with difficulty, form less energetic oxides, and do not decompose water, even at a rather high temperature. Moreover, they only displace hydrogen from very few acids. The difference between them is also seen in the dissimilarity of the properties of many of the corresponding compounds. Thus cuprous oxide, Cu_2O, and silver oxide, Ag_2O, are insoluble in water: the cuprous and silver carbonates, chlorides, and sulphates are also sparingly soluble in water The oxides of silver and copper are also easily reduced to metal. This difference in properties is in intimate relation with that difference in the density of the metals which exists in this case. The alkali metals belong to the lightest, and copper and silver to the heaviest, and therefore the distance between the molecules in these metals is very dissimilar—it is greater for the former than the latter (tables in Chapter XV.). From the point of view of the periodic law, this difference between copper and silver and such elements of Group I. as potassium and rubidium, is clearly seen from the fact that copper and silver

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as that of zinc sulphate, $ZnSO_4,7H_2O$. Supersaturated solutions of each of these salts crystallise in that form and with that amount of water which is contained in a crystal of one or other of the salts brought in contact with th stand in the middle of those large periods (for example, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br) which start with the true metals of the alkalis—that is to say, the analogy and difference between potassium and copper are of the same nature as that between chromium and selenium, or vanadium and arsenic.

Copper is one of the few metals which have long been known in a metallic form. The Greeks and Romans imported copper chiefly from the island of Cyprus—whence its Latin name, *cuprum*. It was known to the ancients before iron, and was used, especially when alloyed with other metals, for arms and domestic utensils. That copper was known to the ancients will be understood from the fact that it occurs, although rarely, in a *native state*, and is easily extracted from its other natural compounds. Among the latter are the oxygen compounds of copper. When ignited with charcoal, they easily give up their oxygen to it, and yield metallic copper; hydrogen also easily takes up the oxygen from copper oxide when heated. Copper occurs in a native state, sometimes in association with other ores, in many parts of the Urals and in Sweden, and in considerable masses in America, especially in the neighbourhood of the great American lakes; and also in Chili, Japan, and China. The oxygen compounds of copper are also of somewhat common occurrence in certain localities; in this respect certain deposits of the Urals are especially famous. The geological period of the Urals (Permian) is characterised by a considerable distribution of copper ores. Copper is met with in the form of *cuprous oxide*, or *suboxide of copper*, Cu_2O, and is then known as *red copper ore*, because it forms red masses which not unfrequently are crystallised in the regular system. It is found much more rarely in the state of *cupric oxide*, CuO, and is then called *black copper ore*. The most common of the oxygenised compounds of copper are the *basic carbonates* corresponding with the oxides. That these compounds are undoubtedly of aqueous origin is apparent, not only from the fact that specimens are frequently found of a gradual transition from the metallic, sulphuretted, and oxidised copper into its various carbonates, but also from the presence of water in their composition, and from the laminar, reniform structure which many of them present. In this respect *malachite* is particularly well known; it is used as a green paint and also for ornaments, owing to the diversity of the shades of colour presented by the different layers of deposited malachite. The composition of malachite corresponds with the basic carbonate containing one molecule of cupric carbonate to one of hydroxide: $CuCO_3,CuH_2O_2$. In this form the copper frequently occurs in admixture with various sediof these compounds. There are many such localities in the Perm and other Governments bounding the Urals. *Blue carbonate of copper*, or *azurite*, is also often met with in the same localities; it contains the same ingredients as malachite, but in a different proportion, its composition being $CuH_2O_2,2CuCO_3$. Both these substances may be obtained artificially by the action of the alkali carbonates on solutions of cupric salts at various temperatures. These native carbonates are often used for the extraction of copper, all the more as they very readily give metallic copper, evolving water and carbonic anhydride when ignited, and leaving the easily-reducible cupric oxide. Copper is, however, still more often met with in the form of the sulphides. The sulphides of copper generally occur in chemical combination with the sulphides of iron.[3] These copper-sulphur compounds (copper pyrites $CuFeS_2$, variegated copper ore Cu_3FeS_3, &c.) generally occur in veins in a rock gangue.

The extraction of copper from its oxide ores does not present any difficulty, because the copper, when ignited with charcoal and melted, is reduced from the impurities which accompany it. This mode of smelting copper ores is carried on in cupola or cylindrical furnaces, fluxes forming a slag being added to the mixture of ore and charcoal.

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[3] Iron pyrites, FeS_2, very often contain a small quantity of copper sulphide (*see* Chapter XXII., Note 2 bis), and on burning the iron pyrites for sulphurous anhydride the copper oxide remains in the residue, from which the copper is often extracted with profit. For this purpose the whole of the sulphur is not burnt off from the iron pyrites, but a portion is left behind in the ore, which is then slowly ignited (roasted) with access of air. Cupric sulphate is then formed, and is extracted by water; or what is better and more frequently done, the residue from the roasting of the pyrites is roasted with common salt, and the solution of cupric chloride obtained by lixiviating is precipitated with iron. A far greater amount of copper is obtained from other sulphuretted ores. Among these *copper glance*, Cu_2S, is more rarely met with. It has a metallic lustre, is grey, generally crystalline, and is obtained in admixture with organic matter; so that there is no doubt that its origin is due to the reducing action of the latter on solutions of cupric sulphate. *Variegated copper ore*, which crystallises in octahedra, not infrequently forms an admixture in copper glance; it has a metallic lustre, and is reddish-brown; it has a superficial play of colours, due to oxidation proceeding on its surface. Its composition is Cu_3FeS_3. But the most common and widely-distributed copper ore is *copper pyrites*, which crystallises in regular octahedra; it has a metallic lustre, a sp. gr. of 4·0, and yellow colour. Its composition is $CuFeS_2$. It must be remarked that the sulphurous ores of copper are oxidised in the presence of water containing oxygen in solution, and form cupric sulphate, blue vitriol, which is easily soluble in water. If this water contains calcium carbonate, gypsum and cupric carbonate are formed by double decomposition: $CuSO_4 + CaCO_3 = CuCO_3 + CaSO_4$. Hence copper sulphide in the form of different ores must be considered as the primary product, and the many other copper ores as secondary products, formed by water. This is confirmed by the fact that at the present time the water extracted from many copper mines contains cupric sulphate in solution. From this liquid it is easy to extract cupric oxide by the action of organic

The smelted copper still contains sulphur, iron, and other metallic impurities, from which it is freed by fusion in reverberatory furnaces, with access of air to the surface of the molten metal, as the iron and sulphur are more easily oxidised than the copper. The iron then separates as oxides, which collect in the slag.[4]

[4] Copper ores rich in oxygen are very rare; the sulphur ores are of more common occurrence, but the extraction of the copper from them is much more difficult. The problem here not only consists in the removal of the sulphur, but also in the removal of the iron combined with the sulphur and copper. This is attained by a whole series of operations, after which there still sometimes remains the extraction of the metallic silver which generally accompanies the copper, although in but small quantity. These processes commence with the roasting—*i.e.* calcination—of the ore with access of air, by which means the sulphur is converted into sulphurous anhydride. It should here be remarked that iron sulphide is more easily oxidised than copper sulphide, and therefore the greater part of the iron in the residue from roasting is no longer in the form of sulphide but of oxide of iron. The roasted ore is mixed with charcoal, and siliceous fluxes, and smelted in a cupola furnace. The iron then passes into the slag, because its oxide gives an easily-fusible mass with the silica, whilst the copper, in the form of sulphide, fuses and collects under the slag. The greater part of the iron is removed from the mass by this smelting. The resultant *coarse metal* is again roasted in order to remove the greater part of the sulphur from the copper sulphide, and to convert the metal into oxide, after which the mass is again smelted. These processes are repeated several times, according to the richness of the ore. During these smeltings a portion of the copper is already obtained in a metallic form, because copper sulphide gives metallic copper with the oxide ($CuS + 2CuO = 3Cu + SO_2$). We will not here describe the furnaces used or the details of this process, but the above remarks include the explanation of those chemical processes which are accomplished in the various technical operations which are made use of in the process (for details *see* works on metallurgy).

Besides the smelting of copper there also exist methods for its extraction from solutions in the wet way, as it is called. Recourse is generally had to these methods for poor copper ores. The copper is brought into solution, from which it is separated by means of metallic iron or by other methods (by the action of an electric current). The sulphides are roasted in such a manner that the greater part of the copper is oxidised into cupric sulphate, whilst at the same time the corresponding iron salts are as far as possible decomposed. This process is based on the fact that the copper sulphides absorb oxygen when they are calcined in the presence of air, forming cupric sulphate. The roasted ore is treated with water, to which acid is sometimes added, and after lixiviation the resultant solution containing copper is treated either with metallic iron or with milk of lime, which precipitates cupric hydroxide from the solution. Copper oxide ores poor in metal may be treated with dilute acids in order to obtain the copper oxides in solution, from which the copper is then easily precipitated either by iron or as hydroxide by lime. According to Hunt and Douglas's method, the copper in the ore is converted by calcination into the cupric oxide, which is brought into solution by the action of a mixture of solutions of ferrous sulphate and sodium chloride; the oxide converts the ferrous chloride into ferric oxide, forming copper chlorides, rding to the equation $3CuO + 2FeCl_2 = CuCl_2 + 2CuCl + Fe_2O_3$. The cupric chloride le in water, whilst the cuprous chloride is dissolved in the solution of sodium nd therefore all the copper passes into solution, from which it is precipitated

llurgists give the following wet method for extracting the es, especially in sulphurous ores: (1) The Cu_2S is in a calciner; (2) the CuO is extracted by the

Copper is characterised by its red colour, which distinguishes it from all other metals. Pure copper is soft, and may be beaten out by a hammer at the ordinary temperature, and when hot may be rolled into very thin sheets. Extremely thin leaves of copper transmit a green light. The tenacity of copper is also considerable, and next to iron it is one of the most durable metals in this respect. Copper wire of 1 sq. millimetre in section only breaks under a weight of 45 kilograms. The specific gravity of copper is 8·8, unless it contains cavities due to the fact that molten copper absorbs oxygen from the air, which is disengaged on cooling, and therefore gives a porous mass whose density is much less. Rolled copper, and also that which is deposited by the electric current, has a comparatively high density. Copper melts at a bright red heat, about 1050°, although below the temperature at which many kinds of cast iron melt. At a high temperature it is converted into vapour, which communicates a green colour to the flame. Both native copper and that cooled from a molten state crystallise in regular octahedra. Copper is not oxidised in dry air at the ordinary temperature, but when calcined it becomes coated with a layer of oxide, and it does not burn even at the highest temperature. Copper, when calcined in air, forms either the red cuprous oxide or the black cupric oxide,

while the Ag, Au and oxides of iron remain behind in the residue (from which the noble metals may be extracted); (3) a portion of the copper in solution is converted into $CuCl_2$ (and $CaSO_4$ precipitated) by means of the $CaCl_2$ obtained in the fifth process; (4) the mixture of solutions of $CuSO_4$ and $CuCl_2$ is converted into the insoluble CuCl (salt of the suboxide) by the action of the SO_2 obtained by roasting the ore (in the first operation), sulphuric acid is then formed in the solution, according to the equation: $CuSO_4 + CuCl_2 + SO_2 + 2H_2O = 2H_2SO_4 + 2CuCl$; (5) the precipitated CuCl is treated with lime and water, and gives $CuCl_2$ in solution and CuO in the residue; and lastly (6) the Cu_2O is reduced to metallic Cu by carbon in a furnace. According to Crooke's method the impure copper regulus obtained by roasting and smelting the ore is broken up and immersed repeatedly in molten lead, which extracts the Ag and Au occurring in the regulus. The regulus is then heated in a reverberatory furnace to run off the lead, and is then smelted for Cu.

The copper brought into the market often contains small quantities of various impurities. Among these there are generally present iron, lead, silver, arsenic, and sometimes small quantities of oxides of copper. As copper, when mixed with a small amount of foreign substances, loses its tenacity to a certain degree, the manufacture of very thin sheet copper requires the use of Chili copper, which is distinguished for its great softness, and therefore when it is desired to have pure copper, it is best to take thin sheet copper, like that which is used in the manufacture of cartridges. But the purest copper is electrolytic copper—that is, that which is deposited from a solution by the action of an electric current.

If the copper contains silver, as is often the case, it is used in gold refineries for the precipitation of silver from its solutions in sulphuric acid. Iron and zinc reduce copper salts, but copper reduces mercury and silver salts. The precipitate contains not only the silver which was previously in solution, but also all that which was in the copper. The silver solutions in sulphuric acid are obtained in the separation of silver from gold by treating their alloys with sulphuric acid, which only dissolves the silver.

according to the temperature and quantity of air supplied. In air at the ordinary temperature, copper—as everyone knows—becomes coated with a brown layer of oxides or a green coating of basic salts, due to the action of the damp air containing carbonic acid. If this action continue for a prolonged time, the copper is covered with a thick coating of basic carbonate, or the so-called verdigris (the *ærugo nobilis* of ancient statues). This is due to the fact that copper, although scarcely capable of oxidising by itself,[5] *in the presence of water and acids*—even very feeble acids, like carbonic acid—*absorbs oxygen from the air and forms salts,* which is a very characteristic property of it (and of lead).[6] *Copper does not decompose water,* and therefore does not disengage hydrogen from it either at the ordinary or at high temperatures. Nor does copper liberate hydrogen from the oxygen acids, these act on it in two ways: they either give up a portion of their oxygen, forming lower grades of oxidation, or else only react in the presence of air. Thus, when nitric acid acts on copper it evolves nitric oxide, the copper being oxidised at the expense of the nitric acid. In the same way copper converts sulphuric acid into the lower grade of oxidation—into sulphurous anhydride, SO_2. In these cases the copper is oxidised to copper oxide, which combines with the excess of acid taken, and therefore forms a cupric salt, CuX_2. Dilute nitric acid does not act on copper at the ordinary temperature, but when heated it reacts with great ease; dilute sulphuric acid does not act on copper except in presence of air.

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[5] Schützenberger showed that when the basic carbonate of copper is decomposed by an electric current it gives, besides the ordinary copper, an allotropic form which grows on the negative platinum electrode, if its surface be smaller than that of the positive copper electrode, in the form of brittle crystalline growths of sp. gr. 8·1. It differs from ordinary copper by giving not nitric oxide but nitrous oxide when treated with nitric acid, and in being very easily oxidised in air, and coated with red shades of colour. It is possible that this is copper hydride, or copper which has occluded hydrogen. Spring (1892) observed that copper reduced from the oxide by hydrogen at the lowest possible temperature was pulverulent, while that reduced from $CuCl_2$ at a somewhat high temperature appeared in bright crystals. The same difference occurs with many other metals, and is probably partly due to the volatility of the metallic chlorides.

[6] This is taken advantage of in practice; for instance, by pouring dilute acids over copper turnings on revolving tables in the preparation of copper salts, such as verdigris, or the basic acetate $2C_4H_6CuO_4,CuH_2O_2,5H_2O$, which is so much used as an oil paint (*i.e.* with boiled oil). The capacity of copper for absorbing oxygen in the presence of acids is so great that it is possible by this means (by taking, for example, thin copper shavings moistened with sulphuric acid) to take up all the oxygen from a given volume of air, and this is even employed for the analysis of air.

The combination of copper with oxygen is not only aided by acids but also by alkalis, although cupric oxide does not appear to have an acid character. Alkalis do not act on copper except in the presence of air, when they produce cupric oxide, which does not appear to combine with such alkalis as caustic potash or soda. But the *action of ammonia* is particularly distinct (Chapter V., Note 2). In the action of a solution of ammonia not only is oxygen absorbed by the copper, but it also acts on the ammonia, and a definite quantity of ammonia is always acted on simultaneously with the passage of the copper into solution. The ammonia is then converted into nitrous acid, according to the reaction: $NH_3+O_3=NHO_2+H_2O$, and the nitrous acid thus formed passes into the state of ammonium nitrite, NH_4NO_2. In this manner three equivalents of oxygen are expended on the oxidation of the ammonia, and six equivalents of oxygen pass over to the copper, forming six atoms of cupric oxide. The latter does not remain in the state of oxide, but combines with the ammonia.

A strong solution of common salt does not act on copper, but a dilute solution of the salt corrodes copper, converting it into oxychloride—that is, in the presence of air. This action of salt water is evident in those cases where the bottoms of ships are coated
eet copper. From what has been said above it will be evident that copper vessels
be employed in the preparation of food, because this contains salts and acids
sence of air, and give copper salts, which are poisonous,
in untinned copper vessels may be poisonous. Hence
is purpose—that is, copper vessels coated with a thin
ne solutions do not act.

Both the oxides of copper, Cu_2O and CuO, are unacted on by air, and, as already mentioned, they both occur in nature.[6 bis] However, in the majority of cases copper is obtained in the form of cupric oxide and its salts—and the copper compounds used industrially generally belong to this type. This is due to the fact that the *cuprous compounds absorb oxygen* from the air and pass into cupric compounds. The cupric compounds may serve as the source for the preparation of cuprous oxide, because many reducing agents are capable of deoxidising the oxide into the suboxide. Organic substances are most generally employed for this purpose, and especially saccharine substances, which are able, in the presence of alkalis, to undergo oxidation at the expense of the oxygen of the cupric oxide, and to give acids which combine with the alkali: $2CuO - O = Cu_2O$. In this case the deoxidation of the copper may be carried further and metallic copper obtained, if only the reaction be aided by heat. Thus, for example, a fine powder of metallic copper may be obtained by heating an ammoniacal solution of cupric oxide with caustic potash and grape sugar. But if the reducing action of the saccharine substance proceed in the presence of a sufficient quantity of alkali in

[6 bis] Copper, besides the cuprous oxide, Cu_2O, and cupric oxide, CuO, gives two known higher forms of oxidation, but they have scarcely been investigated, and even their composition is not well known. *Copper dioxide* (CuO_2, or CuO_2,H_2O, perhaps $CuOH_2O_2$) is obtained by the action of hydrogen peroxide on cupric hydroxide, when the green colour of the latter is changed to yellow. It is very unstable, and is decomposed even by boiling water, with the evolution of oxygen, whilst the action of acids gives cupric salts, oxygen being also disengaged. A still higher *copper peroxide* is formed by heating a mixture of caustic potash, nitre, and metallic copper to a red heat, and by dissolving cupric hydroxide in solutions of the hypochlorites of the alkali metals. A slight heating of the soluble salt formed is enough for it to be decomposed into oxygen and copper dioxide, which is precipitated. Judging from Frémy's researches, the composition of the

solution, and at not too high a temperature, cuprous oxide is obtained. To see this reaction clearly, it is not sufficient to take any cupric salt, because the alkali necessary for the reaction might precipitate cupric oxide—it is necessary to add previously some substance which will prevent this precipitation. Among such substances, tartaric acid, $C_4H_6O_6$, is one of the best. In the presence of a sufficient quantity of tartaric acid, any amount of alkali may be added to a solution of cupric salt without producing a precipitate, because a soluble double salt of cupric oxide and alkali is then formed. If glucose (for instance, honey or molasses) be added to such an alkaline tartaric solution, and the temperature be slightly raised, it first gives a yellow precipitate (this is cuprous hydroxide, CuHO), and then, on boiling, a red precipitate of (anhydrous) cuprous oxide. If such a mixture be left for a long time at the ordinary temperature, it deposits well-formed crystals of anhydrous cuprous oxide belonging to the regular system.[7]

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[7] Colourless solutions of cuprous salts may also be obtained by the action of sulphurous or phosphorous acid and similar lower grades of oxidation on the blue solutions of the cupric salts. This is very clearly and easily effected by means of sodium thiosulphate, $Na_2S_2O_3$, which is oxidised in the process. Cuprous oxide can not only be obtained by the deoxidation of cupric oxide, but also directly from metallic copper itself, because the latter, in oxidising at a red heat in air, first gives cuprous oxide. It is prepared in this manner on a large scale by heating sheet copper rolled into spirals in reverberatory furnaces. Care must be taken that the air is not in great excess, and that the coating of red cuprous oxide formed does not begin to pass into the black cupric oxide. If the oxidised spiral sheet is then unbent, the brittle cuprous oxide falls away from the soft metal. The suboxide obtained in this manner fuses with ease. It is necessary to prevent the access of air during the fusion, and if the mass contains cupric oxide it must be mixed with charcoal, which reduces the latter. Cuprous chloride, CuCl, corresponding with cuprous oxide (as sodium chloride corresponds with sodium oxide), when calcined with sodium carbonate, gives sodium chloride and cuprous oxide, carbonic anhydride being evolved, because it does not combine with the cuprous oxide under these conditions. The reaction can be expressed by the following equation: $2CuCl + Na_2CO_3 = Cu_2O + 2NaCl + CO_2$. The cupric oxide itself, when calcined with finely-divided copper this copper powder may be obtained by many methods—for instance, by immersing zinc in a solution of a copper salt, or by igniting cupric oxide in hydrogen), gives the fusible cuprous oxide: $Cu + CuO = Cu_2O$. Both the native and artificial cuprous oxide have a sp. gr. of 5·6. It is insoluble in water, and is not acted on by (dry) air. When heated with acids the suboxide forms a solution of a cupric salt and metallic copper—for example, $Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$. However, strong hydrochloric acid does not separate metallic copper on dissolving cuprous oxide, which is due to the fact that the cuprous chloride formed is soluble in strong hydrochloric acid. Cuprous oxide also dissolves in a solution of ammonia, and in the absence of air gives a colourless solution, which turns blue in the air, absorbing oxygen, owing to the conversion of the cuprous oxide into cupric oxide. The blue solution thus formed may be again reconverted into a colourless cuprous solution by immersing a copper strip in it, because the metallic copper then deoxidises the cupric oxide in the solution into cuprous oxide. Cuprous oxide is characterised by the fact that it gives red glasses when fused with glass or with salts forming vitreous alloys. Glass tinted with cuprous oxide is used for ornaments. The access of

Cupric chloride, $CuCl_2$, when ignited, gives *cuprous chloride*, $CuCl$ —*i.e.* the salt corresponding with suboxide of copper—and therefore cuprous chloride is always formed when copper enters into reaction with chlorine at a high temperature. Thus, for example, when copper is calcined with mercuric chloride, it forms cuprous chloride and vapours of mercury. The same substance is obtained on heating metallic copper in hydrochloric acid, hydrogen being disengaged; but this reaction only proceeds with finely-divided copper, as hydrochloric acid acts very feebly on compact masses of copper, and, in the presence of air, gives cupric chloride. The green solution of cupric chloride is decolorised by metallic copper, cuprous chloride being formed; but this reaction is only accomplished with ease when the solution is very concentrated and in the presence of an excess of hydrochloric acid to dissolve the cuprous chloride. The addition of water to the solution precipitates the cuprous chloride, because it is less soluble in dilute than in strong hydrochloric acid. Many reducing agents which are able to take up half the oxygen from cupric oxide are able, in the presence of hydrochloric acid, to form cuprous chloride. Stannous salts, sulphurous anhydride, alkali sulphites, phosphorous and hypophosphorous acids, and many similar reducing agents, act in this manner. The usual method of preparing cuprous chloride consists in passing sulphurous anhydride into a very strong solution of cupric chloride: $2CuCl_2 + SO_2 + 2H_2O = 2CuCl + 2HCl + H_2SO_4$. Cuprous chloride forms colourless cubic crystals which are insoluble in water. It is easily fusible, and even volatile. Under the action of oxidising agents, it passes into the cupric salt, and it absorbs oxygen from moist air, forming cupric oxychloride, Cu_2Cl_2O. *Aqueous ammonia easily dissolves* cuprous chloride as well as cuprous oxide; the solution also turns blue on exposure to the air. Thus an ammoniacal solution of cuprous chloride serves as an excellent absorbent for oxygen; but this solution absorbs not only oxygen, but also certain other gases—for example, carbonic oxide and acetylene.[8]

to the formation of cupric oxide, which colours glass blue. This may even be taken advantage of in testing for copper under the blow-pipe by heating the copper compound with borax in the flame of a blow-pipe; a red glass is obtained in the reducing flame, and a blue glass in the oxidising flame, owing to the conversion of the cuprous into cupric oxide.

Étard (1882), by passing sulphurous anhydride into a solution of cupric acetate, obtained a white precipitate of cuprous sulphite, Cu_2SO_3,H_2O, whilst he obtained the same salt, of a red colour, from the double salt of sodium and copper; but there are not any convincing proofs of isomerism in this case.

[8] The solubility of cuprous chloride in ammonia is due to the formation of compounds between the ammonia and the chloride. In a warm solution the compound $NH_3,2CuCl$ is formed, and at the ordinary temperature $CuCl,NH_3$. This salt is soluble in hydro-

When copper is oxidised with a considerable quantity of oxygen at a high temperature, or at the ordinary temperature in the presence of acids, and also when it decomposes acids, converting them into lower grades of oxidation (for example, when submitted to the action of nitric and sulphuric acids), it forms *cupric oxide*, CuO, or, in the presence of acids, cupric salts. Copper rust, or that black mass which forms on the surface of copper when it is calcined, consists of cupric oxide. The coating of the oxidised copper is very easily separated from the metallic copper, because it is brittle and very easily peels off, when it is struck or immersed in water. Many copper salts (for

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nium chloride. By the action of a certain excess of ammonia on a hydrochloric acid solution of cuprous chloride, very well formed crystals, having the composition $CuCl,NH_3,H_2O$, are obtained. Cuprous chloride is not only soluble in ammonia and hydrochloric acid, but it also dissolves in solutions of certain other salts—for example, in sodium chloride, potassium chloride, sodium thiosulphate, and certain others. All the solutions of cuprous chloride act in many cases as very powerful deoxidising substances; for example, it is easy, by means of these solutions, to precipitate gold from its solutions in a metallic form, according to the equation $AuCl_3+3CuCl = Au+3CuCl_2$.

Among the other compounds corresponding with cuprous oxide, *cuprous iodide*, CuI, is worthy of remark. It is a colourless substance which is insoluble in water and sparingly soluble in ammonia (like silver iodide), but capable of absorbing it, and in this respect it resembles cuprous chloride. It is remarkable from the fact that it is exceedingly easily formed from the corresponding cupric compound CuI_2. A solution of cupric iodide easily decomposes into iodine and cuprous iodide, even at the ordinary temperature, whilst cupric chloride only suffers a similar change on ignition. If a solution of a cupric salt be mixed with a solution of potassium iodide the cupric iodide formed immediately decomposes into free iodine and cuprous iodide, which separates out as a precipitate. In this case the cupric salt acts in an oxidising manner, like, for example, nitrous acid, ozone, and other substances which liberate iodine from iodides, but with this difference, that it only liberates half, whilst they set free the whole of the iodine from potassium iodide: $2KI+CuCl_2=2KCl+CuI+I$.

It must also be remarked that cuprous oxide, when treated with hydrofluoric acid, gives an insoluble cuprous fluoride, CuF. Cuprous cyanide is also insoluble in water, and is obtained by the addition of hydrocyanic acid to a solution of cupric chloride saturated with sulphurous anhydride. This cuprous cyanide, like silver cyanide, gives a double soluble salt with potassium cyanide. The double cyanide of copper and potassium is tolerably stable in the air, and enters into double decompositions with various other salts, like those double cyanides of iron with which we are already acquainted.

Copper hydride, CuH, also belongs to the number of the cuprous compounds. It was obtained by Würtz by mixing a hot (70°) solution of cupric sulphate with a solution of hypophosphorous acid, H_3PO_2. The addition of the reducing hypophosphorous acid must be stopped when a brown precipitate makes its appearance, and when gas begins to be evolved. The brown precipitate is the hydrated cuprous hydride. When gently heated it disengages hydrogen; it gives cuprous oxide when exposed to the air, burns in a stream of chlorine, and liberates hydrogen with hydrochloric acid: $CuH+HCl = CuCl+H_2$. Zinc, silver, mercury, lead, and many other heavy metals do not form such a compound with hydrogen, neither under these circumstances nor under the action of hydrogen at the moment of the decomposition of salts by a galvanic current. The greatest resemblance is seen between cuprous hydride and the hydrogen compounds of potassium, sodium, Pd, Ce, and Ba.

instance, the nitrite and carbonate) leave oxide of copper[8 bis] in the form of friable black powder, after being ignited. If the ignition be carried further, Cu_2O may be formed from the CuO.[8 tri] Anhydrous cupric oxide is very easily dissolved in acids, forming cupric salts, CuX_2. They are analogous to the salts MgX_2, ZnX_2, NiX_2, FeX_2, in many respects. On adding potassium or ammonium hydroxide to a solution of a cupric salt, it forms a gelatinous blue precipitate of the hydrated oxide of copper, CuH_2O_2, insoluble in water. The resultant precipitate *is redissolved by an excess of ammonia*, and gives a very beautiful azure blue solution, of so intense a colour that the presence of small traces of cupric salts may be discovered by this means.[9] An excess of

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[8 bis] The oxide of copper obtained by igniting the nitrate is frequently used for organic analyses. It is hygroscopic and retains nitrogen (1·5 c.c. per gram) when the nitrate is heated in vacuo (Richards and Rogers, 1893).

[8 tri] Oxide of copper is also capable of dissociating when heated. Debray and Joannis showed that it then disengages oxygen, whose maximum tension is constant for a given temperature, providing that fusion does not take place (the CuO then dissolves in the molten Cu_2O); that this loss of oxygen is followed by the formation of suboxide, and that on cooling, the oxygen is again absorbed, forming CuO.

[9] Cupric oxide and many of its salts are able to give definite, although unstable, *compounds with ammonia*. This faculty already shows itself in the fact that cupric oxide, as well as the salts of copper, dissolves in aqueous ammonia, and also in the fact that salts of copper absorb ammonia gas. If ammonia be added to a solution of any cupric salt, it first forms a precipitate of cupric hydroxide, which then dissolves in an excess of ammonia. The solution thus formed, when evaporated or on the addition of alcohol, frequently deposits crystals of salts containing both the elements of the salt of copper taken and of ammonia. Several such compounds are generally formed. Thus cupric chloride, $CuCl_2$, according to Deherain, forms four compounds with ammonia—namely, with one, two, four, and six molecules of ammonia. Thus, for example, if ammonia gas be passed into a boiling saturated solution of cupric chloride, on cooling, small octahedral crystals of a blue colour separate out, containing $CuCl_2,2NH_3,H_2O$. At 150° this substance loses half the ammonia and all the water contained in it, leaving the compound $CuCl_2,NH_3$. Nitrate of copper forms the compound $Cu(NO_3)_2,2NH_3$. This compound remains unchanged on evaporation. Dry cupric sulphate absorbs ammonia gas, and gives a compound containing five molecules of ammonia to one of sulphate (Vol. I., p. 257, and Chapter XXII., Note 35). If this compound is dissolved in aqueous ammonia, on evaporation it deposits a crystalline substance containing $CuSO_4,4NH_3,H_2O$. At 150° this substance loses the molecule of water and one-fourth of its ammonia. On ignition all these compounds part with the remaining ammonia in the form of an ammoniacal salt, so that the residue consists of cupric oxide. Both the hydrated and anhydrous cupric oxide are soluble in aqueous ammonia.

The solution obtained by the action of aqueous ammonia and air on copper turnings (Note 6) is remarkable for its faculty *of dissolving cellulose*, which is insoluble in water, dilute acids, and alkalis. Paper soaked in such a solution acquires the property of not rotting, of being difficultly combustible, and waterproof, &c. It has therefore been applied, especially in England, to many practical purposes—for example, to the construction of temporary buildings, for covering roofs, &c. The composition of the substance held in solution is $Cu(HO)_2,4NH_3$.

If dry ammonia gas be passed over cupric oxide heated to 265°, a portion of the oxide of copper remains unaltered, whilst the other portion gives *copper nitride*, the oxygen of the copper oxide combining with the hydrogen and forming water. The oxide of copper which remains unchanged is easily removed by washing the resultant product with potassium or sodium hydroxide does not dissolve cupric hydroxide. A hot solution gives a black precipitate of the anhydrous oxide instead of the blue precipitate, and the precipitate of the hydroxide of copper becomes granular, and turns black when the solution is heated. This is due to the fact that the blue hydroxide is exceedingly unstable, and when slightly heated it loses the elements of water and gives the black anhydrous cupric oxide: $CuH_2O_2 = CuO + H_2O$.

Cupric oxide fuses at a strong heat, and on cooling forms a heavy crystalline mass, which is black, opaque, and somewhat tenacious. It is a feebly energetic base, so that not only do the oxides of the metals of the alkalis and alkaline earths displace it from its compounds, but even such oxides as those of lead and silver precipitate it from solutions, which is partially due to these oxides being soluble, although but slightly so, in water. However, cupric oxide, and especially the hydroxide, easily combines with even the least energetic acids, and does not give any compounds with bases; but, on the other hand, *it easily forms basic salts,*[9 bis] and in this respect outstrips magnesium and recalls the

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aqueous ammonia. Copper nitride is very stable, and is insoluble; it has the composition Cu_3N (*i.e.* the copper is monatomic here as in Cu_2O), and is an amorphous green powder, which is decomposed when strongly ignited, and gives cuprous chloride and ammonium chloride when treated with hydrochloric acid. Like the other nitrides, copper nitride, Cu_3N, has scarcely been investigated. Granger (1892), by heating copper in the vapour of phosphorus, obtained hexagonal prisms of Cu_5P, which passed into Cu_6P (previously obtained by Abel) when heated in nitrogen. Arsenic is easily absorbed by copper, and its presence (like P), even in small quantities, has a great influence upon the properties of copper—for instance, pure copper wire 1 sq. mm. in section breaks under a load of 35 kilos, while the presence of 0·22 p.c. of arsenic raises the breaking load to 42 kilos.

[9 bis] As a comparatively feeble base, oxide of copper easily forms both basic and double salts. As an instance we may mention the double salts composed of the dichloride $CuCl_2,2H_2O$ and potassium chloride. The double salt $CuK_2Cl_4,2H_2O$ crystallises from solutions in *blue* plates, but when heated alone or with substances taking up water easily gives *brown* needles $CuKCl_3$ and at the same time KCl, and this reaction is reversible at 92° as Meyerhoffer (1889) showed (*i.e.* above 92° the simpler double salt is formed and below 92° the more complex salt). With an excess of the copper salt, KCl gives another double salt, $Cu_2KCl_5,4H_2O$, the transition temperature of which is 55°. The instances of equilibria which are encountered in such complex relations (*see* Chapter XIV., Note 25, astrakhanite, and Chapter XXII., Note 28) are embraced by the *law of phases* given by Gibbs (Transactions of the Connecticut Academy of Sciences, 1875–1878, in J. Willard Gibbs' memoir 'On the equilibrium of heterogeneous substances:' and in a clearer and more accessible form in H. W. Bakhuis Roozeboom's papers, Rec. trav. chim., Vol. VI., and in W. Meyerhoffer's memoir *Die Phasenregel und ihre Anwendungen*, 1893, to which sources we refer those desiring fuller information respecting this law). Gibbs calls '*bodies*' substances (simple or compound) capable of forming homogeneous complexes (for instance, solutions or intercombinations) of a varied composition; a *phase*—a mechanically separable portion of such bodies or of their homogeneous complexes (for instance, a vapour, liquid or precipitated

oxides of lead or mercury. Hence the hydroxide of copper dissolve solutions of neutral cupric salts. The cupric salts are generally blue green, because cupric hydroxide itself is coloured. But some of salts in the anhydrous state are colourless.[10]

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characterised by a constant pressure at a constant temperature even under a chang the amount of one of the component parts (for instance, of a salt in a saturated soluti while an *imperfect equilibrium* is such a one for which such a change corresponds w a change of pressure (for instance, an unsaturated solution). The law of phases cons in the fact that: *n bodies only give a perfect equilibrium when n + 1 phases partici in that equilibrium*—for example, in the equilibrium of a salt in its saturated solut in water there are two bodies (the salt and water) and three phases, namely, the s solution, and vapour, which can be mechanically separated from each other, and to t equilibrium there corresponds a definite tension. At the same time, *n bodies m occur in n + 2 phases, but only at one definite temperature and one pressure*; a cha of one of these may bring about another state (perfect or not—equilibrium stable unstable). Thus water when liquid at the ordinary temperature offers two pha (liquid and vapour) and is in perfect equilibrium (as also is ice below 0°), but water, and vapour (three phases and only one body) can only be in equilibrium at 0°, and at ordinary pressure; with a change of *t* there will remain either only ice and vapour only liquid water and vapour; whilst with a rise of pressure not only will the vap pass into the liquid (there again only remain two phases) but also the temperature the formation of ice will fall (by about 7° per 1000 atmospheres). The same laws phases are applicable to the consideration of the formation of simple or double sa from saturated solutions and to a number of other purely chemical relations. Thus, example, in the above-mentioned instance, when the bodies are KCl, $CuCl_2$, and H perfect equilibrium (which here has reference to the solubility) consisting of four phas corresponds to the following seven cases, considering only the phases (above A = $CuCl_2,2KCl,2H_2O$; B = $CuCl_2KCl$; C = $CuCl_2,2H_2O,KCl$, solution and vapo (1) A + B + solution + vapour; (2) A + C + solution + vapour; (3) A + KCl + solut + vapour; (4) A + B + C + vapour (it follows that B + KCl + solution gives A); A + C + KCl + vapour; (6) B + C + solution + vapour; and (7) B + KCl + solution + vapo Thus above 92° A gives B + KCl. The law of phases by bringing complex instances chemical reaction under simple physical schemes, facilitates their study in detail a gives the means of seeking the simplest chemical relations dealing with solutions, d sociation, double decompositions and similar cases, and therefore deserves consideratio but a detailed exposition of this subject must be looked for in works on physi chemistry.

[10] The normal *cupric nitrate*, $CuN_2O_6,3H_2O$, is obtained as a deliquescent salt of a bl colour (soluble in water and in alcohol) by dissolving copper or cupric oxide in nitric ac It is so easily decomposed by the action of heat that it is impossible to drive off the wat of crystallisation from it before it begins to decompose. During the ignition of the norm salt the cupric oxide formed enters into combination with the remaining undecompos normal salt, and gives a basic salt, $CuN_2O_6,2CuH_2O_2$. The same basic salt is obtain if a certain quantity of alkali or cupric hydroxide or carbonate be added to the soluti of the normal salt, which is even decomposed when boiled with metallic copper, and for the basic salt as a green powder, which easily decomposes under the action of heat a leaves a residue of cupric oxide. The basic salt, having the composition $CuN_2O_6,3CuH_2$ is nearly insoluble in water.

The normal *carbonate of copper*, $CuCO_3$, occurs in nature, although extremely rarel If solutions of cupric salts be mixed with solutions of alkali carbonates, then, as in t case of magnesium, carbonic anhydride is evolved and basic salts are formed, which va in composition according to the temperature and conditions of the reaction. By mixi cold solutions, a voluminous blue precipitate is formed, containing an equivalent pr

The commonest normal salt is *blue vitriol*—*i.e.* the normal cupric sulphate. It generally contains five molecules of water of crystallisation, $CuSO_4,5H_2O$. It forms the product of the action of strong sulphuric acid on copper, sulphurous anhydride being evolved. The same salt is obtained in practice by carefully roasting sulphuretted ores of copper, and also by the action of water holding oxygen in solution on them : $CuS + O_4 = CuSO_4$. This salt forms a by-product, obtained in gold refineries, when the silver is precipitated from the sulphuric acid solution by means of copper. It is also obtained by pouring dilute sulphuric acid over sheet copper in the presence of air, or by heating cupric oxide or carbonate in sulphuric acid. The crystals of this salt belong to the triclinic system, have a specific gravity of 2·19, are of a beautiful blue colour, and give a solution of the same colour. 100 parts of water at 0° dissolve 15, at 25° 23, and at 100° about 45 parts of cupric sulphate, $CuSO_4$.[10 bis] At 100° this salt loses a portion of its

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is the same as malachite, sp. gr. 3·5): $2CuSO_4 + 2Na_2CO_3 + H_2O = CuCO_3,CuH_2O_2 + 2Na_2SO_4 + CO_2$. If the resultant blue precipitate be heated in the liquid, it loses water and is transformed into a granular green mass of the composition Cu_2CO_4—*i.e.* into a compound of the normal salt with anhydrous cupric oxide. This salt of the oxide corresponds with orthocarbonic acid, $C(OH)_4 = CH_4O_4$, where 4H is replaced by 2Cu. On further boiling this salt loses a portion of the carbonic acid, forming black cupric oxide, so unstable is the compound of copper with carbonic anhydride. Another basic salt which occurs in nature, $2CuCO_3,CuH_2O_2$, is known as azurite, or blue carbonate of copper; it also loses carbonic acid when boiled with water. On mixing a solution of cupric sulphate with sodium sesquicarbonate no precipitate is at first obtained, but after boiling a precipitate is formed having the composition of malachite. Debray obtained artificial azurite by heating cupric nitrate with chalk.

[10 bis] Although sulphate of copper usually crystallises with $5H_2O$, that is, differently to the sulphates of Mg, Fe, and Mn, it is nevertheless perfectly isomorphous with them, as is seen not only in the fact that it gives isomorphous mixtures with them, containing a similar amount of water of crystallisation, but also in the ease with which it forms, like all bases analogous to MgO, double salts, $R_2Cu(SO_4)_2,6H_2O$, where R = K, Rb, Cs, of the monoclinic system.

Salts of this kind, like $CuCl_2,2KCl,2H_2O,PtK_2Cy_4$, *&c.*, present a composition CuX_2 if the representation of double salts given in Chapter XXIII., Note 11, be admitted, because they, like $Cu(HO)_2$, contain $Cu(X_2K)_2$, where $X_2 = SO_4$, *i.e.* the residue of sulphuric acid, which combines with H_2, and is therefore able to replace the H_2 by X_2 or O. A detailed study of the crystalline forms of these salts, made by Tutton (1893) (*see* Chapter XIII., Note 1), showed: (1) that 22 investigated salts of the composition $R_2M(SO_4),6H_2O$, where R = K, Rb, Cs, and M = Mg, Zn, Cd, Mn, Fe, Co, Ni, Cu, present a complete crystallographic resemblance; (2) that in all respects the Rb salts present a transition between the K and Cs salts; (3) that the Cs salts form crystals most easily, and the K salts the most difficultly, and that for the K salts of Cd and Mn it was even impossible to obtain well-formed crystals; (4) that notwithstanding the closeness of their angles, the general appearance (habit) of the potassium compound differs very clearly from the Cs salts, while the Rb salts present a distinct transition in this respect; (5) that the angle of the inclination of one of the axes to the plane of the two other axes showed that in the K salts (angle from 75° to 75° 38′) the inclination is least, in the Cs salts (from 72° 52′ to 73° 50′) greatest, and in the Rb salts (from 73° 57′ to 74° 42′) intermediate between the two; the replacement of Mg. . . Cu produces but a water of crystallisation, which it only parts with entirely at a high temperature (220°) and then gives a white powder of the anhydrous sulphate; and the latter, on further calcination, loses the elements of sulphuric anhydride, leaving cupric oxide, like all the cupric salts. The anhydrous (colourless) cupric sulphate is sometimes used for absorbing water; it turns blue in the process. It offers the advantage that it retains both hydrochloric acid and water, but not carbonic anhydride.[11] Cupric sulphate is used for steeping seed corn; this is said to prevent the growth of certain parasites on the plants. In the arts a considerable quantity of cupric sulphate is also used in the preparation of other copper salts—for instance, of certain pigments[11 bis]—and a particularly

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very small change in this angle; (6) that the other angles and the ratio of the axes of the crystals exhibit a similar variation; and (7) that thus the variation of the form is chiefly determined by the atomic weight of the alkaline metal. As an example we cite the magnitude of the inclination of the axes of $R_2M(SO_4)_2,6H_2O$.

R =	K	Rb	Cs
M = Mg	75° 12′	74° 1′	72° 54′
Zn	75° 12′	74° 7′	72° 59′
Cd	—	74° 7′	72° 49′
Mn	—	73° 8′	72° 53′
Fe	75° 28′	74° 16′	73° 8′
Co	75° 5′	73° 59′	72° 52′
Ni	75° 0′	73° 57′	72° 53′
Cu	75° 32′	74° 42′	73° 50′

This shows clearly (within the limits of possible error, which may be as much as 30′) the almost perfect identity of the independent crystalline forms notwithstanding the difference of the atomic weights of the diatomic elements, M = Mg . . . Cu.

[11] In addition to what has been said (Chapter I., Note 65, and Chapter XXII., Note 35) respecting the combination of $CuSO_4$ with water and ammonia, we may add that Lachinoff (1893) showed that $CuSO_4,5H_2O$ loses $4\frac{1}{2}H_2O$ at 130°, that $CuSO_4,5NH_3$ also loses $4\frac{1}{2}NH_3$ at 320°, and that only $\frac{1}{2}H_2O$ and $\frac{1}{2}NH_3$ remain in combination with the $CuSO_4$. The last $\frac{1}{2}H_2O$ can only be driven off by heating to 200°, and the last $\frac{1}{2}NH_3$ by heating to 360° Ammonia displaces water from $CuSO_4,5H_2O$, but water cannot displace the ammonia from $CuSO_4,5NH_3$. If hydrochloric acid gas be passed over $CuSO_4,5H_2O$ at the ordinary temperature, it first forms $CuSO_4,5H_2O,3HCl$, and then $CuSO_4,2H_2O,2HCl$. When air is passed over the latter compound it passes into $CuSO_4H_2O$ with a small amount of HCl (about $\frac{1}{3}HCl$). At 100°, $CuSO_4,5H_2O$ in a stream of hydrochloric acid gas gives $CuSO_4,\frac{1}{2}H_2O,2HCl$, and then $CuSO_4,\frac{1}{2}H_2OHCl$, whilst after prolonged heating $CuSO_4$ remains, which rapidly passes into $CuSO_4,5H_2O$ when placed under a bell jar over water. Over sulphuric acid, however, $CuSO_4,5H_2O$ only parts with $3H_2O$, and if $CuSO_4,2H_2O$ be placed over water it again forms $CuSO_4,5H_2O$, and so on.

[11 bis] Commercial blue vitriol generally contains ferrous sulphate. The salt is purified by converting the ferrous salt into a ferric salt by heating the solution with chlorine or nitric acid. The solution is then evaporated to dryness, and the unchanged cupric sulphate extracted from the residue, which will contain the larger portion of the ferric oxide. The remainder will be separated if cupric hydroxide is added to the solution and boiled; the cupric oxide, CuO, then precipitates the ferric oxide, Fe_2O_3, just as it is itself precipitated by silver oxide. But the solution will contain a small proportion of a basic salt of copper, and therefore sulphuric acid must be added to the filtered solution, and the salt allowed to crystallise. Acid salts are not formed, and cupric sulphate itself has an acid reaction on litmus paper.

large quantity is used *in the galvanoplastic process*, which consists in the deposition of copper from a solution of cupric sulphate by the action of a galvanic current, when the metallic copper is deposited on the negative pole and takes the shape of the latter. The description of the processes of galvanoplastic art introduced by Jacobi in St. Petersburg forms a part of applied physics, and will not be touched on here, and we will only mention that, although first introduced for small articles, it is now used for such articles as type moulds (*clichés*), for maps, prints, &c., and also for large statues, and for the deposition of iron, zinc, nickel, gold, silver, &c. on other metals and materials. The beginning of the application of the galvanic current to the practical extraction of metals from solutions has also been established, especially since the dynamo-electric machines of Gramme, Siemens, and others have rendered it possible to cheaply convert the mechanical motion of the steam engine into an electric current. It is to be expected that the application of the electric current, which has long since given such important results in chemistry, will, in the near future, play an important part in technical processes, the example being shown by electric lighting.

The alloys of copper with certain metals, and especially with zinc and tin, are easily formed by directly melting the metals together. They are easily cast into moulds, forged, and worked like copper, whilst they are much more durable in the air, and are therefore frequently used in the arts. Even the ancients used exclusively alloys of copper, and not pure copper, but its alloys with tin or different kinds of bronze (Chapter XVIII., Note 35). The alloys of copper with zinc are called *brass* or 'yellow metal.' Brass contains about 32 p.c. of zinc; generally, however, it does not contain more than 65 p.c. of copper. The remainder is composed of lead and tin, which usually occur, although in small quantities, in brass. Yellow metal contains about 40 p.c. of zinc.[12] The addition of zinc to copper changes the colour of the latter to a considerable degree; with a certain amount of zinc the colour of the copper becomes yellow, and with a still larger proportion of zinc an alloy is formed which has a greenish tint In those alloys of zinc and copper which contain a larger amount of zinc than of copper, the yellow colour disappears and is replaced by a greyish colour. But when the amount of zinc is diminished to about 20 p.c., the alloy is red and hard, and is called 'tombac.' A contraction takes place in alloying copper with zinc, so that the volume of the alloy is less than that of either metal individually. The zinc volatilises on prolonged heating at a high temperature and the excess of metallic copper remains behind. When heated in the air, the zinc oxidises before the copper, so that all the zinc alloyed with copper may be removed from the copper by this means. An important property of brass containing about 30 p.c. of zinc is that it is soft and malleable in the cold, but becomes somewhat brittle when heated. We may also mention that ordinary copper coins contain, in order to render them hard, tin, zinc, and iron ($Cu = 95$ p.c.); that it is now customary to add a small amount of phosphorus to copper and bronze, for the same purpose; and also that copper is added to silver and gold in coining, &c. to render it hard; moreover, in Germany, Switzerland, and Belgium, and other countries, a silver-white alloy (melchior, German silver, &c.), for base coinage and other purposes, is prepared from brass and nickel (from 10 to 20 p.c. of nickel; 20 to 30 p.c. zinc: 50 to 70 p.c. copper), or directly from copper and nickel, or, more rarely, from an alloy containing silver, nickel, and copper.[12 bis]

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[12] Among the alloys of copper resembling brass, *delta metal*, invented by A. Dick (London) is largely used (since 1883). It contains 55 p.c. Cu, and 41 p.c. Zn, the remaining 4 p.c. being composed of iron (as much as 8½ p.c., which is first alloyed with zinc), or of cobalt, and manganese, and certain other metals. The sp. gr. of delta metal is 8·4. It melts at 950°, and then becomes so fluid that it fills up all the cavities in a mould and forms excellent castings. It has a tensile strength of 70 kilos per sq. mm. (gun metal about 20, phosphor bronze about 30). It is very soft, especially when heated to 600°, but after forging and rolling it becomes very hard; it is more difficultly acted upon by air and water than other kinds of brass, and preserves its golden yellow colour for any length of time, especially if well polished. It is used for making bearings, screw propellers, valves, and many other articles. In general the alloys of Cu and Zn containing about ⅔ p.c. by weight of copper were for a long time almost exclusively made in Sweden and England (Bristol, Birmingham). These alloys for the most part are cheaper, harder, and more fusible than copper alone, and form good castings. The alloys con-

Copper, in its cuprous compounds, is so analogous to *silver*, that

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taining 45–80 p.c. Cu crystallise in cubes if slowly cooled (Bi also gives crystals). By washing the surface of brass with dilute sulphuric acid, Zn is removed and the article acquires the colour of copper. The alloys approaching Zn_4Cu_5 in their composition exhibit the greatest resistance (under other equal conditions; of purity, forging, rolling, &c.) The addition of 3 p.c. Al, or 5 p.c. Sn, improves the quality of brass. Respecting aluminium bronze *see* Chapter XVII. p. 88.

[12 bis] Ball (also Kamensky), 1888, by investigating the electrical conductivity of the alloys of antimony and copper with lead, came to the conclusion that only two definite compounds of antimony and copper exist, whilst the other alloys are either alloys of these two together or with antimony or with copper. These compounds are Cu_2Sb and Cu_4Sb—one corresponds with the maximum, and the other with the minimum, electrical resistance. In general, the resistance offered to an electrical current forms one of the methods by which the composition of definite alloys (for example, Pb_2Zn_7) is often established, whilst the electromotive force of alloys affords (Laurie, 1888) a still more accurate method—for instance, several definite compounds were discovered by this method among the alloys of copper with zinc and tin; but we will not enter into any details of this subject, because we avoid all references to electricity, although the reader is recommended to make himself acquainted with this branch of science, which has many points in common with chemistry. The study of alloys regarded as solid solutions should, in my opinion, throw much light upon the question of solutions, which is still obscure in many aspects and in many branches of chemistry.

were there no cupric compounds, or if silver gave stable compounds of the higher oxide, AgO, the resemblance would be as close as that between chlorine and bromine or zinc and cadmium; but silver compounds corresponding to AgO are quite unknown. Although silver peroxide—which was regarded as AgO, but which Berthelot (1880) recognised as the sesquioxide Ag_2O_3—is known, still it does not form any true salts, and consequently cannot be placed along with cupric oxide. In distinction to copper, silver as a metal does not oxidise under the influence of heat; and its oxides, Ag_2O and Ag_2O_3, easily lose oxygen (*see* Note 8 tri). Silver does *not oxidise* in air at the ordinary pressure, and is therefore classed among the so-called *noble metals*. It has a white colour, which is much purer than that of any other known metal, especially when the metal is chemically pure. In the arts silver is always used alloyed, because chemically-pure silver is so soft that it wears exceedingly easily, whilst when fused with a small amount of copper, it becomes very hard, without losing its colour.[13]

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[13] There are not many soft metals; lead, tin, copper, silver, iron, and gold are somewhat soft, and potassium and sodium very soft. The metals of the alkaline earths are sonorous and hard, and many other metals are even brittle, especially bismuth and antimony. But the very slight significance which these properties have in determining the fundamental chemical properties of substances (although, however, of immense importance in the practical applications of metals) is seen from the example shown by zinc, which is hard at the ordinary temperature, soft at 100°, and brittle at 200°.

As the value of silver depends exclusively on its purity, and as there is no possibility of telling the amount of impurities alloyed with it from its external appearance, it is customary in most countries to mark an article with the amount of pure silver it contains after an accurately-made analysis known as the assay of the silver. In France the assay of silver shows the amount of pure silver in 1,000 parts by weight; in Russia the amount of pure silver in 96 parts—that is, the assay shows the number of zolotniks (4·26 grams) of pure silver in one pound (410 grams) of alloyed silver. Russian silver is generally 84 assay—that is, contains 84 parts by weight of pure silver and 12 parts of copper and other metals. French money contains 90 p.c. (in the Russian system this will be 86·4 assay) by weight of silver [English coins and jewellery contain 92·5 p.c. of silver]; the silver rouble is of 83⅓ assay—that is, it contains 86·8 p.c. of silver—and the smaller Russian silver coinage is of 48 assay, and therefore contains 50 p.c. of silver. Silver ornaments and articles are usually made in Russia of 84 and 72 assay. As the alloys of silver and copper, especially after being subjected to the action of heat, are

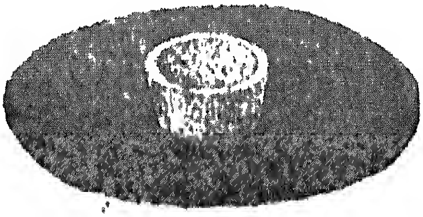

FIG. 95.—Cupel for silver assaying.

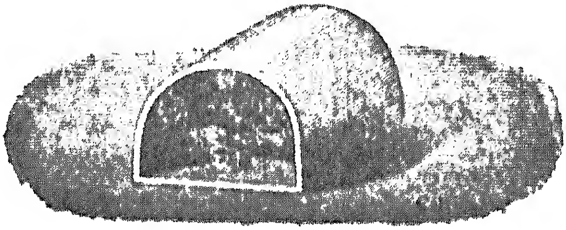

FIG. 96.—Clay muffle.

Silver occurs *in nature*, both in a native state and in certain compounds. Native silver, however, is of rather rare occurrence. A far

'pickling') after being worked up. This consists in removing the copper from the surface of the article by subjecting it to a dark-red heat and then immersing it in dilute acid. During the calcination the copper on the surface is oxidised, whilst the silver remains unchanged; the dilute acid then dissolves the copper oxides formed, and pure silver is left on the surface. The surface is dull after this treatment, owing to the removal of a portion of the metal by the acid. After being polished the article acquires the desired lustre and colour, so as to be indistinguishable from a pure silver object. In order to test a silver article, a portion of its mass must be taken, not from the surface, but to a certain depth. The methods of assay used in practice are very varied. The commonest and most often used is that known as *cupellation*. It is based on the difference in the oxidisability of copper, lead, and silver. The cupel is a porous cup with thick sides, made by compressing bone ash. The porous mass of bone ash absorbs the fused oxides, especially the lead oxide, which is easily fusible, but it does not absorb the unoxidised metal. The latter collects into a globule under the action of a strong heat in the cupel, and on cooling solidifies into a button, which may then be weighed. Several cupels are placed in a muffle. A muffle is a semi-cylindrical clay vessel, shown in the accompanying drawing. The sides of the muffle are pierced with several orifices, which allow the access of air into it. The muffle is placed in a furnace, where it is strongly heated. Under the action of the air entering the muffle the copper of the silver alloy is oxidised, but as the oxide of copper is infusible, or, more strictly speaking, difficultly fusible, a certain quantity of lead is added to the alloy; the lead is also oxidised by the air at the high temperature of the muffle, and gives the very fusible lead oxide. The copper oxide then fuses with the lead oxide, and is absorbed by the cupel, whilst the silver remains as a

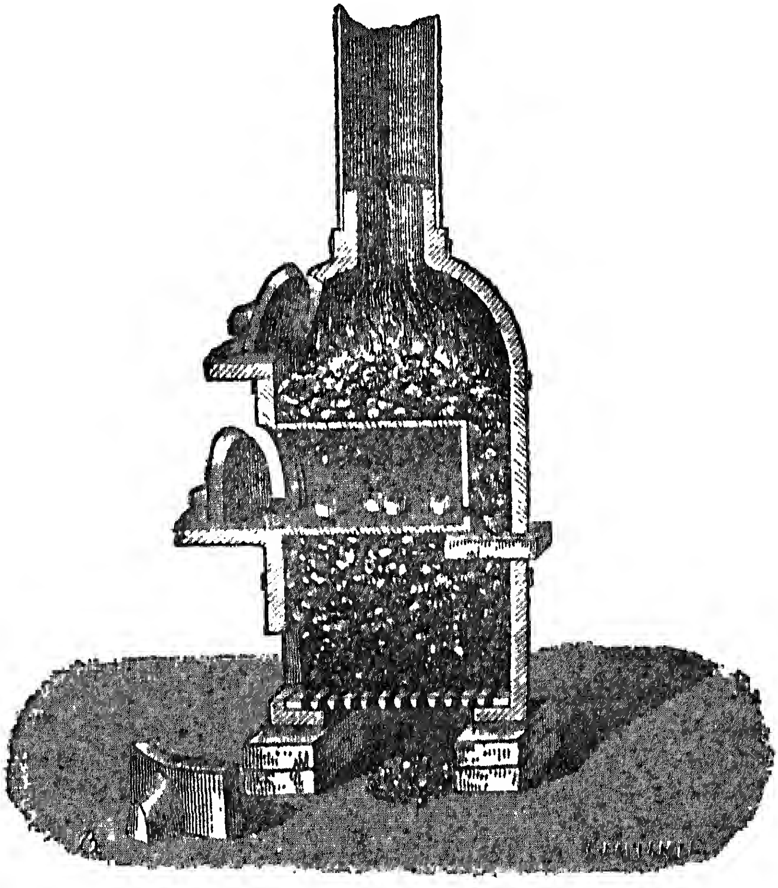

Fig. 97.—Portable muffle furnace

greater quantity of silver occurs in combination with sulphur, and especially in the form of *silver sulphide*, Ag_2S, with lead sulphide or copper sulphide, or the ores of various other metals. The largest amount of silver is extracted from the lead in which it occurs. If this lead be calcined in the presence of air, it oxidises, and the resultant lead oxide, PbO ('litharge' or 'silberglätte,' as it is called), melts into a mobile liquid, which is easily removed. The silver remains in an unoxidised metallic state.[14] This process is called *cupellation*.

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bright white globule. If the weight of the alloy taken and of the silver left on the cupel be determined, it is possible to calculate the composition of the alloy. Thus the essence of cupellation consists in the separation of the oxidisable metals from silver, which does not oxidise under the action of heat. A more accurate method, based on the precipitation of silver from its solutions in the form of silver chloride, is described in detail in works on analytical chemistry.

[14] In America, whence the largest amount of silver is now obtained, ores are worked containing not more than $\frac{1}{4}$ p.c. of silver, whilst at $\frac{1}{2}$ p.c. its extraction is very profitable. Moreover, the extraction of silver from ores containing not more than 0·01 p.c. of this metal is sometimes profitable. The majority of the lead smelted from galena contains silver, which is extracted from it. Thus near Arras, in France, an ore is worked which contains about 65 parts of lead and 0·088 part of silver in 100 parts of ore, which corresponds with 136 parts of silver in 100,000 parts of lead. At Freiberg, in Saxony, the ore used (enriched by mechanical dressing) contains about 0·9 of silver, 160 of lead, and 2 of copper in 10,000 parts. In every case the lead is first extracted in the manner described in Chapter XVIII., and this lead will contain all the silver. Not unfrequently other ores of silver are mixed with lead ores, in order to obtain an argentiferous lead as the product. The extraction of small quantities of silver from lead is facilitated by the fact (Pattinson's process) that molten argentiferous lead in cooling first deposits crystals of pure lead, which fall to the bottom of the cooling vessel, whilst the proportion of silver in the unsolidified mass increases owing to the removal of the crystals of lead. The lead is enriched in this manner until it contains $\frac{1}{200}$ part of silver, and is then subjected to cupellation on a larger scale. According to Park's process, zinc is added to the molten argentiferous lead, and the alloy of Pb and Zn, which first separates out on cooling, is collected. This alloy is found to contain all the silver previously contained in the lead. The addition of 0·5 p.c. of aluminium to the zinc (Rossler and Edelman) facilitates the extraction of the Ag from the resultant alloy besides preventing oxidation; for, after re-melting, nearly all the lead easily runs off (remains fluid), and leaves an alloy containing about 30 p.c. Ag and about 70 p.c. Zn. This alloy may be used as an anode in a solution of $ZnCl_2$, when the Zn is deposited on the cathode, leaving the silver with a small amount of Pb, &c. behind. The silver can be easily obtained pure by treating it with dilute acids and cupelling.

The ores of silver which contain a larger amount of it are: silver glance, Ag_2S (sp. gr. 7·2); argentiferous-copper glance, CuAgS; horn silver or chloride of silver, AgCl; argentiferous grey copper ore; polybasite, M_9RS_6 (where $M = Ag, Cu_2$ and $R = Sb, As$), and argentiferous gold. The latter is the usual form in which gold is found in alluvial deposits and ores. The crystals of gold from the Beresoffsky mines in the Urals contain 90 to 95 of gold and 5 to 9 of silver, and the Altai gold contains 50 to 65 of gold and 36 to 38 of silver. The proportion of silver in native gold varies between these limits in other localities. Silver ores, which generally occur in veins, usually contain native silver and various sulphur compounds. The most famous mines in Europe are in Saxony (Freiberg), which has a yearly output of as much as 26 tons of silver, Hungary, and Bohemia (41 tons). In Russia, silver is extracted in the Altai and at Nerchinsk (17 tons). The richest silver mines known are in America, especially in Chili (as much as 70 tons), Mexico (200 tons), and more particularly in the Western States of North America. The

Commercial silver generally contains copper, and, more rarely, other metallic impurities also. Chemically *pure silver* is obtained either by cupellation or by subjecting ordinary silver to the following treatment. The silver is first dissolved in nitric acid, which converts it and the copper into nitrates, $Cu(NO_3)_2$ and $AgNO_3$; hydrochloric acid is then added to the resultant solution (green, owing to the presence of the cupric salt), which is considerably diluted with water in order to retain the lead chloride in solution if the silver contained lead. The copper and many other metals remain in solution, whilst the silver is precipitated as silver chloride. The precipitate is allowed to settle, and the liquid is decanted off; the precipitate is then washed and fused with sodium carbonate. A double decomposition then takes place, sodium chloride and silver carbonate being formed; but the latter decomposes into metallic silver, because the silver oxide is decomposed by heat: $Ag_2CO_3 = Ag_2 + O + CO_2$. The silver chloride may also be mixed with metallic zinc, sulphuric acid, and water, and left for some time, when the zinc removes the chlorine from the silver chloride and precipitates the silver as a powder. This finely-divided silver is called 'molecular silver.'[15]

richness of these mines may be judged from the fact that one mine in the State of Nevada (Comstock, near Washoe and the cities of Gold Hill and Virginia), which was discovered in 1859, gave an output of 400 tons in 1866. In place of cupellation, chlorination may also be employed for extracting silver from its ores. The method of chlorination consists in converting the silver in an ore into silver chloride. This is either done by a wet or by a dry method, roasting the ore with NaCl. When the silver chloride is formed, the extraction of the metal is also done by two methods. The first consists in the silver chloride being reduced to metal by means of iron in rotating barrels, with the subsequent addition of mercury which dissolves the silver, but does not act on the other metals. The mercury holding the silver in solution is distilled, when the silver remains behind. This method is called *amalgamation*. The other method is less frequently used, and consists in dissolving the silver chloride in sodium chloride or in sodium thiosulphate, and then precipitating the silver from the solution. The amalgamation is then carried on in rotating barrels containing the roasted ore mixed with water, iron, and mercury. The iron reduces the silver chloride by taking up the chlorine from it. The technical details of these processes are described in works on metallurgy. The extraction of AgCl by the wet method is carried on (Patera's process) by means of a solution of hyposulphite of sodium which dissolves AgCl (*see* Note 28), or by lixiviating with a 2 p.c. solution of a double hyposulphite of Na and Cu (obtained by adding $CuSO_4$ to $Na_2S_2O_3$). The resultant solution of AgCl is first treated with soda to precipitate $PbCO_3$, and then with Na_2S, which precipitates the Ag and Au. The process should be carried on rapidly to prevent the precipitation of Cu_2S from the solution of $CuSO_4$ and $Na_2S_2O_3$.

[15] There is another practical method which is also suitable for separating the silver from the solutions obtained in photography, and consists in precipitating the silver by oxalic acid. In this case the amount of silver in the solution must be known, and 23 grams of oxalic acid dissolved in 400 grams of water must be added for every 60 grams of silver in solution in a litre of water. A precipitate of silver oxalate, $Ag_2C_2O_4$, is then obtained, which is insoluble in water but soluble in acids. Hence, if the liquid contains any free acid it must be previously freed from it by the addition of sodium carbonate

Chemically-pure silver has an exceeding pure white colour, and a specific gravity of 10·5. Solid silver is lighter than the molten metal, and therefore a piece of silver floats on the latter. The fusing-point of silver is about 950° C., and at the high temperature attained by the combustion of detonating gas it volatilises.[16] By employing silver reduced from silver chloride by milk sugar and caustic potash, and distilling it, Stas obtained silver purer than that obtained by any other means; in fact, this was perfectly pure silver. The vapour of silver has a very beautiful green colour, which is seen when a silver wire is placed in an oxyhydrogen flame.[17]

It has long been known (Wöhler) that when nitrate of silver, $AgNO_3$, reacts as an oxidising agent upon citrates and tartrates, it is able under certain conditions to give either a salt of suboxide of silver (see Note 19) or a red solution, or to give a precipitate of metallic silver reduced at the expense of the organic substances. In 1889 Carey Lea, in his researches on this class of reactions, showed that *soluble*

The resultant precipitate of silver oxalate is dried, mixed with an equal weight of dry sodium carbonate, and thrown into a gently-heated crucible. The separation of the silver then proceeds without an explosion, whilst the silver oxalate if heated alone decomposes with explosion.

According to Stas, the best method for obtaining silver from its solutions is by the reduction of silver chloride dissolved in ammonia by means of an ammoniacal solution of cuprous thiosulphate; the silver is then precipitated in a crystalline form. A solution of ammonium sulphite may be used instead of the cuprous salt.

[16] Silver is very malleable and ductile; it may be beaten into leaves 0·002 mm. in thickness. Silver wire may be made so fine that 1 gram is drawn into a wire 2½ kilometres long. In this respect silver is second only to gold. A wire of 2 mm. diameter breaks under a strain of 20 kilograms.

[17] In melting, silver absorbs a considerable amount of oxygen, which is disengaged on solidifying. One volume of molten silver absorbs as much as 22 volumes of oxygen. In solidifying, the silver forms cavities like the craters of a volcano, and throws off metal, owing to the evolution of the gas; all these phenomena recall a volcano on a miniature scale (Dumas). Silver which contains a small quantity of copper or gold, &c., does not show this property of dissolving oxygen.

The absorption of oxygen by molten silver is, however, an oxidation, but it is at the same time a phenomenon of solution. One cubic centimetre of molten silver can dissolve twenty-two cubic centimetres of oxygen, which, even at 0°, only weighs 0·03 gram, whilst 1 cubic centimetre of silver weighs at least 10 grams, and therefore it is impossible to suppose that the absorption of the oxygen is attended by the formation of any definite compound (rich in oxygen) of silver and oxygen (about 45 atoms of silver to 1 of oxygen) in any other but a dissociated form, and this is the state in which substances in solution must be regarded (Chapter I.)

Le Chatelier showed that at 300° and 15 atmospheres pressure silver absorbs so much oxygen that it may be regarded as having formed the compound Ag_4O, or a mixture of Ag_2 and Ag_2O. Moreover, silver oxide, Ag_2O, only decomposes at 300° under low pressures, whilst at pressures above 10 atmospheres there is no decomposition at 300° but only at 400°.

Stas showed that silver is oxidised by air in the presence of acids. V. d. Pfordten confirmed this, and showed that an acidified solution of potassium permanganate rapidly dissolves silver in the presence of air.

silver is here formed, which he called *allotropic silver.* It may be obtained by taking 200 c.c. of a 10 per cent. solution of $AgNO_3$ and quickly adding a mixture (neutralised with NaHO) of 200 c.c. of a 80 per cent. solution of $FeSO_4$ and 200 c.c. of a 40 per cent. solution of sodium citrate. A lilac precipitate is obtained, which is collected on a filter (the precipitate becomes blue) and washed with a solution of NH_4NO_3. It then becomes soluble in pure water, forming a red perfectly transparent solution from which the dissolved silver is precipitated on the addition of many soluble foreign bodies. Some of the latter—for instance, NH_4NO_3, alkaline sulphates, nitrates, and citrates—give a precipitate which redissolves in pure water, whilst others—for instance, $MgSO_4$, $FeSO_4$, $K_2Cr_2O_7$, $AgNO_3$, $Ba(NO_3)_2$ and many others—convert the precipitated silver into a new variety, which, although no longer soluble in water, regains its solubility in a solution of borax, and is soluble in ammonia. Both the soluble and insoluble silver are rapidly converted into the ordinary grey-metallic variety by sulphuric acid, although nothing is given off in the reaction; the same change takes place on ignition, but in this case CO_2 is disengaged; the latter is formed from the organic substances which remain (to the amount of 3 per cent.) in the modified silver (they are not removed by soaking in alcohol or water). If the precipitated silver be slightly washed and laid in a smooth thin layer on paper or glass, it is seen that the soluble variety is red when moist and a fine blue colour when dry, whilst the insoluble variety has a blue reflex. Besides these, under special conditions[18] a golden yellow variety may be obtained, which gives a brilliant golden yellow coating on glass; but it is easily converted into the ordinary grey-metallic state by friction or trituration. There is no doubt [18 bis] that there is the same relation between ordinary silver which is perfectly insoluble in water and the varieties of silver obtained by Carey Lea [18 tri] as there is between quartz and soluble silica or between

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[18] When solutions of $AgNO_3$, $FeSO_4$, sodium citrate, and NaHO are mixed together in the manner described above, they throw down a precipitate of a beautiful lilac colour; when transferred to a filter paper the precipitate soon changes colour, and becomes dark blue. To obtain the substance as pure as possible it is washed with a 5–10 p.c. solution of ammonium nitrate; the liquid is decanted, and 150 c.c. of water poured over the precipitate. It then dissolves entirely in the water. A small quantity of a saturated solution of ammonium nitrate is added to the solution, and the silver in solution again separates out as a precipitate. These alternate solutions and precipitations are repeated seven or eight times, after which the precipitate is transferred to a filter and washed with 95 p.c. alcohol until the filtrate gives no residue on evaporation. An analysis of the substance so obtained showed that it contained from 97·18 p.c. to 97·31 p.c. of metallic silver. It remained to discover what the remaining 2–3 p.c. were composed of. Are they merely impurities, or is the substance some compound of silver with oxygen or hydrogen, or does it contain citric acid in combination which might account for its solubility? The first supposition is set aside by the fact that no gases are disengaged by the precipitate of silver, either under the action of gases or when heated. The second supposition is shown to be impossible by the fact that there is no definite relation between the silver and citric acid. A determination of the amount of silver in solution showed that the amount of citric acid varies greatly for one and the same amount of silver, and there is no simple ratio between them. Among other methods of preparing soluble silver given by Carey Lea, we may mention the method published by him in 1891. $AgNO_3$ is added to a solution of dextrine in caustic soda or potash; at first a precipitate of brown oxide of silver is thrown down, but the

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brown colour then changes into a reddish chocolate, owing to the reduction of the silver by the dextrine, and the solution turns a deep red. A few drops of this solution turn water bright red, and give a perfectly transparent liquid. The dextrine solution is prepared by dissolving 40 grams of caustic soda and the same amount of ordinary brown dextrine in two litres of water. To this solution is gradually added 28 grams of $AgNO_3$ dissolved in a small quantity of water.

The insoluble allotropic silver is obtained, as was mentioned above, from a solution of silver prepared in the manner described, by the addition of sulphate of copper, iron, barium, magnesium, &c. In one experiment Lea succeeded in obtaining the insoluble allotropic Ag in a crystalline form. The red solution, described above, after standing several weeks, deposits crystals spontaneously in the form of short black needles and thin prisms, the liquid becoming colourless. This insoluble variety, when rubbed upon paper, has the appearance of bright shining green flakes, which polarise light.

The gold variety is obtained in a different manner to the two other varieties. A solution is prepared containing 200 c.c. of a 10 p.c. solution of nitrate of silver, 200 c.c. of a 20 p.c. solution of Rochelle salt, and 800 c.c. of water. Just as in the previous case the reaction consisted in the reduction of the citrate of silver, so in this case it consists in the reduction of the tartrate, which here first forms a red, and then a black precipitate of allotropic Ag, which, when transferred to the filter, appears of a beautiful bronze colour. After washing and drying, this precipitate acquires the lustre and colour peculiar to polished gold, and this is especially remarked where the precipitate comes into contact with glass or china. An analysis of the golden variety gave a percentage composition of 98·750 to 98·749 Ag. Both the insoluble varieties (the blue and gold) have a different specific gravity from ordinary silver. Whilst that of fused silver is 10·50, and of finely-divided silver 10·62, the specific gravity of the blue insoluble variety is 9·58, and of the gold variety 8·51. The gold variety passes into ordinary Ag with great ease. This transition may even be remarked on the filter in those places which have accidentally not been moistened with water. A simple shock, and therefore friction of one particle upon another, is enough to convert the gold variety into normal white silver. Carey Lea sent samples of the gold variety for a long distance by rail packed in three tubes, in which the silver occupied about the quarter of their volume; in one tube only he filled up this space with cotton-wool. It was afterwards found that the shaking of the particles of Ag had completely converted it into ordinary white silver, and that only the tube containing the cotton-wool had preserved the golden variety intact.

The soluble variety of Ag also passes into the ordinary state with great ease, the heat of conversion being, as Prange showed in 1890, about +60 calories.

[18 bis] The opinion of the nature of soluble silver given below was first enunciated in the *Journal of the Russian Chemical Society*, February 1, 1890, Vol. XXII., Note 78. This view is, at the present time, generally accepted, and this silver is frequently known as the 'colloid' variety. I may add that Carey Lea observed the solution of ordinary molecular silver in ammonia without the access of air.

[18 tri] It is, however, noteworthy that ordinary metallic lead has long been considered soluble in water, that boron has been repeatedly obtained in a brown solution, and that observations upon the development of certain bacteria have shown that the latter die in water which has been for some time in contact with metals. This seems to indicate the passage of small quantities of metals into water (however, the formation of peroxide of

CuS and As_2S_2 in their ordinary insoluble forms and in the state of the colloid solution of their hydrosols (*see* Chapter I., Note 57, and Chapter XVII., Note 25 bis). Here, however, an important step in advance has been made in this respect, that we are dealing with the solution of a simple body, and moreover of a metal—*i.e.* of a particularly characteristic state of matter. And as boron, gold, and certain other simple bodies have already been obtained in a soluble (colloid) form, and as numerous organic compounds (albuminous substances, gum, cellulose, starch, &c.) and inorganic substances are also known in this form, it might be said that the colloid state (of hydrogels and hydrosols) can be acquired, if not by every substance, at all events by substances of most varied chemical character under particular conditions of formation from solutions. And this being the case, we may hope that a further study of soluble colloid compounds, which apparently present various transitions towards emulsions, may throw a new light upon the complex question of solutions, which forms one of the problems of the present epoch of chemical science. Moreover, we may remark that Spring (1890) clearly proved the colloid state of soluble silver by means of dialysis as it did not pass through the membrane.

As regards the capacity of silver for chemical reactions, it is remarkable for its small capacity for combination with oxygen and for its considerable energy of combination with sulphur, iodine, and certain kindred non-metals. *Silver does not oxidise* at any temperature, and its oxide, Ag_2O, is decomposed by heat. It is also a very important fact that silver is not oxidised by oxygen either in the presence of alkalis, even at exceedingly high temperatures, or in the presence of acids—at least, of dilute acids—which properties render it a very important metal in chemical industry for the fusion of alkalis, and also for many purposes in everyday life; for instance, for making spoons, salt-cellars, &c. Ozone, however, oxidises it. Of all acids nitric acid has the greatest action on silver. The reaction is accompanied by the formation of oxides of nitrogen and silver nitrate, $AgNO_3$, which dissolves in water and does not, therefore, hinder the further action of the acid on the metal. The halogen acids, especially hydriodic acid, act on silver, hydrogen being evolved; but this action soon stops, owing to the halogen compounds of silver being insoluble in water and only very slightly soluble in acids; they therefore preserve the remaining mass of metal from the further action of the acid; in consequence of this the action of the halogen acids is only distinctly seen with finely-divided silver. Sulphuric acid acts on silver in the same manner that it does on copper, only it must be concentrated and at a higher temperature. Sulphurous anhydride and not hydrogen is then evolved but there is no action at the ordinary temperature, even in the presence of air. Among the various salts, sodium chloride (in the presence of moisture, air, and carbonic acid) and potassium cyanide (in the presence of air) act on silver more decidedly than any others, converting it respectively into silver chloride and a double cyanide.

Although silver does not directly combine with oxygen, still three different grades of combination with oxygen may be obtained indirectly from the salts of silver. They are all, however, unstable, and decompose into oxygen and metallic silver when ignited. These three oxides of silver have the following composition: *silver suboxide*, Ag_4O,[19] corresponding with the (little investigated) suboxides of the alkali metals; *silver oxide*, Ag_2O, corresponding with the oxides of the alkali metals and the ordinary salts of silver, AgX; and *silver peroxide*, AgO,[19 bis] or, judging from Berthelot's researches, Ag_2O_3. *Silver oxide* is obtained as a brown precipitate (which when dried does not contain water) by adding potassium hydroxide to a solution of a silver salt—for example, of silver nitrate. The precipitate formed seems, however,

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[19] Silver suboxide (Ag_4O) or argentous oxide is obtained from argentic citrate by heating it to 100° in a stream of hydrogen. Water and argentous citrate are then formed, and the latter, although but slightly soluble in water, gives a reddish-brown solution of colloid silver (Note 18), and when boiled this solution becomes colourless and deposits metallic silver, the argentic salt being again formed. Wöhler, who discovered this oxide, obtained it as a black precipitate by adding potassium hydroxide to the above solution of argentous citrate. With hydrochloric acid the suboxide gives a brown compound, Ag_2Cl. Since the discovery of soluble silver the above data cannot be regarded as perfectly trustworthy; it is probable that a mixture of Ag_2 and Ag_2O was being dealt with, so that the actual existence of Ag_4O is now doubtful, but there can be no doubt as to the formation of a subchloride, Ag_2Cl (*see* Note 25), corresponding to the suboxide. The same compound is obtained by the action of light on the higher chloride. Other acids do not combine with silver suboxide, but convert it into an argentic salt and metallic silver. In this respect cuprous oxide presents a certain resemblance to these suboxides. But copper forms a suboxide of the composition Cu_4O, which is obtained by the action of an alkaline solution of stannous oxide on cupric hydroxide, and is decomposed by acids into cupric salts and metallic copper. The problems offered by the suboxides, as well as by the peroxides, cannot be considered as fully solved.

[19 bis] *Silver peroxide*, AgO or Ag_2O_3, is obtained by the decomposition of a dilute (10 p.c.) solution of silver nitrate by the action of a galvanic current (Ritter). On the positive pole, where oxygen is usually evolved in the decomposition of salts, brittle grey needles with a metallic lustre, which occasionally attain a somewhat considerable size, are then formed. They are insoluble in water, and decompose with the evolution of oxygen when they are dried and heated, especially up to 150°, and, like lead dioxide, barium peroxide, &c., their action is strongly oxidising. When treated with acids, oxygen is evolved and a salt of the oxide formed. Silver peroxide absorbs sulphurous anhydride and forms silver sulphate. Hydrochloric acid evolves chlorine; ammonia reduces the silver, and is itself oxidised, forming water and gaseous nitrogen. Analyses of the above-mentioned crystals show that they contain silver nitrate, peroxide, and water. According to Fisher, they have the composition $4AgO,AgNO_3,H_2O$, and, according to Berthelot,

to be an hydroxide, AgHO, *i.e.* $AgNO_3 + KHO = KNO_3 + AgHO$, and the formation of the anhydrous oxide, $2AgHO = Ag_2O + H_2O$, may be compared with the formation of the anhydrous cupric oxide by the action of potassium hydroxide on hot cupric solutions. Silver hydroxide decomposes into water and silver oxide, even at low temperatures; at least, the hydroxide no longer exists at 60°, but forms the anhydrous oxide, Ag_2O.[19 tri] Silver oxide is almost insoluble in water; but, nevertheless, it is undoubtedly a rather powerful basic oxide, because it displaces the oxides of many metals from their soluble salts, and saturates such acids as nitric acid, forming with them neutral salts, which do not act on litmus paper.[20] Undoubtedly water dissolves a small quantity of silver oxide, which explains the possibility of its action on solutions of salts—for example, on solutions of cupric salts. Water in which silver oxide is shaken up has a distinctly alkaline reaction. The oxide is distinguished by its great instability when heated, so that it loses all its oxygen when slightly heated. Hydrogen reduces it at about 80°.[20 bis] The feebleness of the affinity of silver for oxygen is shown by the fact that silver oxide decomposes under the action of light, so that it must be kept in opaque vessels. The silver *salts* are colourless and decompose when heated, leaving metallic silver if the elements of the acid are volatile.[20 tri] They have a peculiar metallic taste, and are exceedingly poisonous; the majority of them are acted on by light, especially in the presence of organic substances, which are then oxidised. The alkaline carbonates give a white precipitate of silver carbonate, Ag_2CO_3, which is insoluble in water, but soluble in ammonia and ammonium carbonate. Aqueous ammonia, added to a solution of a normal silver salt, first acts like potassium hydroxide, but the precipitate dissolves in an excess of the reagent, like the precipitate of cupric

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[19 tri] According to Carey Lea, however, oxide of silver still retains water even at 100°, and only parts with it together with the oxygen. Oxide of silver is used for colouring glass yellow.

[20] The reaction of $Pb(OH)_2$ upon AgHO in the presence of NaHO leads to the formation of a compound of both oxides, $PbOnAg_2O$, from which the oxide of lead cannot be removed by alkalies (Wöhler, Leton). Wöhler, Welch, and others obtained crystalline double salts, R_2AgX_3, by the action of strong solutions of RX of the halogen salts of the alkaline metals upon AgX, where R = Cs, Rb, K.

[20 bis] According to Müller, ferric oxide is reduced by hydrogen (see Chapter XXII., Note 5) at 295° (into what ?), cupric oxide at 140°, Ni_2O_3 at 150°; nickelous oxide, NiO, is reduced to the suboxide, Ni_2O, at 195°, and to nickel at 270°; zinc oxide requires so high a temperature for its reduction that the glass tube in which Müller conducted the experiment did not stand the heat; antimony oxide requires a temperature of 215° for its reduction; yellow mercuric oxide is reduced at 130° and the red oxide at 230°; silver oxide at 85°, and platinum oxide even at the ordinary temperature.

[20 tri] A silica compound, Ag_2OSiO_2 is obtained by fusing $AgNO_3$ with silica; this salt is able to decompose with the evolution of oxygen, leaving $Ag + SiO_2$.

hydroxide.[21] Silver oxalate and the halogen compounds of silver are insoluble in water; hydrochloric acid and soluble chlorides give, as already repeatedly observed, a white precipitate of silver chloride in solutions of silver salts. Potassium iodide gives a yellowish precipitate of silver iodide. Zinc separates all the silver in a metallic form from solutions of silver salts. Many other metals and reducing agents—for example, organic substances—also reduce silver from the solutions of its salts.

Silver nitrate, $AgNO_3$, is known by the name of lunar caustic (or *lapis infernalis*); it is obtained by dissolving metallic silver in nitric acid. If the silver be impure, the resultant solution will contain a mixture of the nitrates of copper and silver. If this mixture be evaporated to dryness and the residue carefully fused at an incipient red heat, all the cupric nitrate is decomposed, whilst the greater part of the silver nitrate remains unchanged. On treating the fused mass with water the latter is dissolved, whilst the cupric oxide remains insoluble. If a certain amount of silver oxide be added to the solution containing the nitrates of silver and copper, it displaces all the cupric oxide. In this case it is of course not necessary to take pure silver oxide, but only to pour off some of the solution and to add potassium hydroxide to one portion, and to mix the resultant precipitate of the hydroxides, $Cu(OH)_2$ and $AgOH$, with the remaining portion.[22] By these methods all the copper can be easily removed and pure silver nitrate obtained (its solution is colourless, while the presence of Cu renders it blue), which may be ultimately purified by crystallisation. It crystallises in colourless transparent prismatic plates, which are not acted on by air. They are anhydrous. Its sp. gr. is 4·34; it dissolves in half its weight of water at the ordinary temperature.[22 bis] The pure salt is not acted on by light, but it easily acts in an oxidising manner on the majority of organic substances, which it generally blackens. This is due to the fact that the organic substance is oxidised by the silver nitrate, which is reduced to metallic silver; the latter is thus obtained in a finely-divided state, which causes the black stain. This peculiarity is taken advantage of for marking linen. Silver nitrate is for the same reason used for *cauterising wounds* and various growths on the body. Here again it acts by virtue of its oxidising capacity in destroying the organic matter, which it oxidises, as is seen from the separation of a coating of black metallic powdery silver from the part cauterised.[22 tri] From the description of the preparation of silver nitrate it will have been seen that this salt, which fuses at 218°, does not

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[21] If a solution of a silver salt be precipitated by sodium hydroxide, and aqueous ammonia is added drop by drop until the precipitate is completely dissolved, the liquid when evaporated deposits a violet mass of crystalline silver oxide. If moist silver oxide be left in a strong solution of ammonia it gives a black mass, which easily decomposes with a loud explosion, especially when struck. This black substance is called fulminating silver. Probably this is a compound like the other compounds of oxides with ammonia, and in exploding the oxygen of the silver oxide forms water with the hydrogen of the ammonia, which is naturally accompanied by the evolution of heat and formation of gaseous nitrogen, or, as Raschig states, fulminating silver contains NAg_3 or one of the amides (for instance, $NHAg_2 = NH_3 + Ag_2O - H_2O$). Fulminating silver is also formed when potassium hydroxide is added to a solution of silver nitrate in ammonia. The dangerous explosions which are produced by this compound render it needful that great care be taken when salts of silver come into contact with ammonia and alkalis (see Chapter XVI., Note 26).

[22] So that we here encounter the following phenomena: copper displaces silver from the solutions of its salts, and silver oxide displaces copper oxide from cupric salts. Guided by the conceptions enunciated in Chapter XV., we can account for this in the following manner: The atomic volume of silver = 10·3, and of copper = 7·2, of silver oxide = 32, and of copper oxide = 13. A greater contraction has taken place in the formation of cupric oxide, CuO, than in the formation of silver oxide, Ag_2O, since in the former (13 − 7 = 6) the volume after combination with the oxygen has increased by very little, whilst the volume of silver oxide is considerably greater than that of the metal it contains [32 − (2 × 10·3) = 11·4]. Hence silver oxide is less compact than cupric oxide, and is therefore less stable; but, on the other hand, there are greater intervals

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give more stable compounds than those of copper oxide. This is verified by the figures and data of their reactions. It is impossible to calculate for cupric nitrate, because this salt has not yet been obtained in an anhydrous state; but the sulphates of both oxides are known. The specific gravity of copper sulphate in an anhydrous state is 3·53, and of silver sulphate 5·36; the molecular volume of the former is 45, and of the latter 58. The group SO_3 in the copper occupies, as it were, a volume 45 − 13 = 32, and in the silver salt a volume 58 − 32 = 26; hence a smaller contraction has taken place in the formation of the copper salt from the oxide than in the formation of the silver salt, and consequently the latter should be more stable than the former. Hence silver oxide is able to decompose the salt of copper oxide, whilst with respect to the metals both salts have been formed with an almost identical contraction, since 58 volumes of the silver salt contain 21 volumes of metal (difference = 37), and 45 volumes of the copper salt contain 7 volumes of copper (difference = 38). Besides which, it must be observed that copper oxide displaces iron oxide, just as silver oxide displaces copper oxide. Silver, copper, and iron, in the form of oxides, displace each other in the above order, but in the form of metals in a reverse order (iron, copper, silver). The cause of this order of the displacement of the oxides lies, amongst other things, in their composition. They have the composition Ag_2O, Cu_2O_2, Fe_2O_3; the oxide containing a less proportion of oxygen displaces that containing a larger proportion, because the basic character diminishes with the increase of contained oxygen.

Copper also displaces mercury from its salts. It may here be remarked that Spring (1888), on leaving a mixture of dry mercurous chloride and copper for two hours, observed a distinct reduction, which belongs to the category of those phenomena which demonstrate the existence of a mobility of parts (*i.e.* atoms and molecules) in solid substances.

[22 bis] The reaction of 1 part by weight of $AgNO_3$ requires (according to Kremers) the following amounts of water: at 0°, 0·82 part, at 19°·5, 0·41 part, at 54°, 0·20 part, at 110°, 0·09 part, and, according to Tilden, at 125°, 0·0617 part, and at 133°, 0·0515 part.

[22 tri] It may be remarked that the black stain produced by the reduction of metallic silver disappears under the action of a solution of mercuric chloride or of potassium cyanide, because these salts act on finely-divided silver.

se at an incipient red heat; when cast into sticks it is usually
d for cauterising. On further heating, the fused salt undergoes
sition, first forming silver nitrite and then metallic silver.
mmonia, silver nitrate forms, on evaporation of the solution,
ss crystals containing $AgNO_3,2HN_3$ (Marignac). In general
of silver, like cuprous, cupric, zinc, &c. salts, are able to give
compounds with ammonia; for example, silver nitrate in a dry
sorbs three molecules (Rose). The ammonia is generally easily
from these compounds by the action of heat.
ate of silver easily forms double salts like $AgNO_3 2NaNO_3$ and
KNO_3. Silver nitrate under the action of water and a halogen
tric acid (*see* Vol. I. p. 280, formation of N_2O_5), a halogen salt of
nd a silver salt of an oxygen acid of the halogen. Thus, for
, a solution of chlorine in water, when mixed with a solution of
itrate, gives silver chloride and chlorate. It is here evident that
tion of the silver nitrate is identical with the reaction of the
alkalis, as the nitric acid is all set free and the silver oxide only
n exactly the same way in which aqueous potash acts on free
. Hence the reaction may be expressed in the following
: $6AgNO_3 + 3Cl_2 + 3H_2O = 5AgCl + AgClO_3 + 6NHO_3$.
er nitrate, like the nitrates of the alkalis, does not contain any
of crystallisation. Moreover the other salts of silver almost
separate out without any water of crystallisation. The silver
re further characterised by the fact that they *give neither
nor acid salts*, owing to which the formation of silver salts
ly forms the means of determining the true composition of
thus, to any acid H_nX there corresponds a salt Ag_nX—for
, Ag_3PO_4 (Chapter XIX., Note 15).
er gives insoluble and exceedingly stable *compounds with the
s*. They are obtained by double decomposition with great
whenever a silver salt comes in contact with halogen salts.
ns of nitrate, sulphate, and all other kindred salts of silver give
pitate of silver chloride or iodide in solutions of chlorides and
and of the halogen acids, because the halogen salts of silver are
le both in water[23] and in other acids. *Silver chloride*, AgCl, is

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lver chloride is almost perfectly insoluble in water, but is somewhat soluble in
ntaining sodium chloride or hydrochloric acid, or other chlorides, and many salts,
on. Thus at 100°, 100 parts of water saturated with sodium chloride dissolve
of silver chloride. Bromide and iodide of silver are less soluble in this respect,
n regard to other solvents. It should be remarked that *silver chloride dissolves
ions of ammonia, potassium cyanide, and of sodium thiosulphate*, $Na_2S_2O_3$.
romide is almost perfectly analogous to the chloride, but silver iodide is nearly
e in a solution of ammonia. Silver chloride even absorbs dry ammonia gas

then obtained as a white flocculent precipitate, silver bromide forms a yellowish precipitate, and silver iodide has a very distinct yellow colour. These halogen compounds sometimes occur in nature; they are formed by a dry method—by the action of halogen compounds on silver compounds, especially under the influence of heat. Silver chloride easily fuses at 451° on cooling from a molten state; it forms a somewhat soft horn-like mass which can be cut with a knife and is known as *horn silver*. It volatilises at a higher temperature. Its ammoniacal solution, on the evaporation of the ammonia, deposits crystalline chloride of silver, in octahedra. Bromide and iodide of silver also appear in forms of the regular system, so that in this respect the halogen salts of silver resemble the halogen salts of the alkali metals.[24]

forming very unstable ammoniacal compounds. When heated, these compounds (Vol. I. p. 250, Note 8) evolve the ammonia, as they also do under the action of all acids. Silver chloride enters into double decomposition with potassium cyanide, forming a soluble double cyanide, which we shall presently describe; it also forms a soluble double salt, $NaAgS_2O_3$, with sodium thiosulphate.

Silver chloride offers different modifications in the structure of its molecule, as is seen in the variations in the consistency of the precipitate, and in the differences in the action of light which partially decomposes AgCl (*see* Note 25). Stas and Carey Lea investigated this subject, which has a particular importance in photography, because silver bromide also gives *photo-salts*. There is still much to be discovered in this respect, since Abney showed that perfectly dry AgCl placed in a vacuum in the dark is not in the least acted upon when subsequently exposed to light.

[24] *Silver bromide* and *iodide* (which occur as the minerals bromite and iodite) resemble the chloride in many respects, but the degree of affinity of silver for iodine is greater than that for chlorine and bromine, although less heat is evolved (*see* Note 28 bis). Deville deduced this fact from a number of experiments. Thus silver chloride, when treated with hydriodic acid, evolves hydrochloric acid, and forms silver iodide. Finely-divided silver easily liberates hydrogen when treated with hydriodic acid; it produces the same decomposition with hydrochloric acid, but in a considerably less degree and only on the surface. The difference between silver chloride and iodide is especially remarkable, since the formation of the former is attended with a greater contraction than that of the latter. The volume of AgCl = 26; of chlorine 27, of silver 10, the sum = 37, hence a contraction has ensued; and in the formation of silver iodide an expansion takes place, for the volume of Ag is 10, of I 26, and of AgI 39 instead of 36 (density, AgCl, 5·59; AgI, 5·67). The atoms of chlorine have united with the atoms of silver without moving asunder, whilst the atoms of iodine must have moved apart in combining with the silver. It is otherwise with respect to the metal; the distance between its atoms in the metal = 2·2, in silver chloride = 3·0, and in silver iodide = 3·5; hence its atoms have moved asunder considerably in both cases. It is also very remarkable, as Fizeau observed, that the density of silver iodide increases with a rise of temperature—that is, a contraction takes place when it is heated and an expansion when it is cooled.

In order to explain the fact that in silver compounds the iodide is more stable than the chloride and oxide, Professor N. N. Beketoff, in his 'Researches on the Phenomena of Substitutions' (Kharkoff, 1865), proposed the following original hypothesis, which we will give in almost the words of the author:—In the case of aluminium, the oxide, Al_2O_3, is more stable than the chloride, Al_2Cl_6, and the iodide, Al_2I_6. In the oxide the amount of the metal is to the amount of the element combined with it as 54·6 (Al = 27·3) is to 48, Silver chloride may be decomposed, with the separation of silver oxide, by heating it with a solution of an alkali, and if an organic

or in the ratio 112 : 100; for the chloride the ratio is = 25 : 100; for the iodide it = 7 : 100 In the case of silver the oxide (ratio = 1350 : 100) is less stable than the chloride (ratio = 304 : 100), and the iodide (ratio of the weight of metal to the weight of the halogen = 85 : 100) is the most stable. From these and similar examples it follows that the most stable compounds are those in which the weights of the combined substances are equal. This may be partly explained by the attraction of similar molecules even after their having passed into combination with others. This attraction is proportional to the product of the acting masses. In silver oxide the attraction of Ag_2 for $Ag_2 = 216 \times 216 = 46{,}656$, and the attraction of Ag_2 for $O = 216 \times 16 = 3{,}456$. The attraction of like molecules thus counteracts the attraction of the unlike molecules. The former naturally does not overcome the latter, otherwise there would be a disruption, but it nevertheless diminishes the stability. In the case of an equality or proximity of the magnitude of the combining masses, the attraction of the like parts will counteract the stability of the compound to the least extent—in other words, with an inequality of the combined masses, the molecules have an inclination to return to an elementary state, to decompose, which does not exist to such an extent where the combined masses are equal. There is, therefore, a tendency for large masses to combine with large, and for small masses to combine with small. Hence $Ag_2O + 2KI$ gives $K_2O + 2AgI$. The influence of an equality of masses on the stability is seen particularly clearly in the effect of a rise of temperature. Argentic, mercuric, auric and other oxides composed of unequal masses, are somewhat readily decomposed by heat, whilst the oxides of the lighter metals (like water) are not so easily decomposed by heat. Silver chloride and iodide approach the condition of equality, and are not decomposed by heat. The most stable oxides under the action of heat are those of magnesium, calcium, silicon, and aluminium, since they also approach the condition of equality. For the same reason hydriodic acid decomposes with greater facility than hydrochloric acid. Chlorine does not act on magnesia or alumina, but it acts on lime and silver oxide, &c. This is partially explained by the fact that by considering heat as a mode of motion, and knowing that the atomic heats of the free elements are equal, it must be supposed that the amount of the motion of atoms (their *vis viva*) is equal, and as it is equal to the product of the mass (atomic weight) into the square of the velocity, it follows that the greater the combining weight the smaller will be the square of the velocity, and if the combining weights be nearly equal, then the velocities also will be nearly equal. Hence the greater the difference between the weights of the combined atoms the greater will be the difference between their velocities. The difference between the velocities will increase with the temperature, and therefore the temperature of decomposition will be the sooner attained the greater be the original difference—that is, the greater the difference of the weights of the combined substances. The nearer these weights are to each other, the more analogous the motion of the unlike atoms, and consequently, the more stable the resultant compound.

The instability of cupric chloride and nitric oxide, the absence of compounds of fluorine with oxygen, whilst there are compounds of oxygen with chlorine, the greater stability of the oxygen compounds of iodine than those of chlorine, the stability of boron nitride, and the instability of cyanogen, and a number of similar instances, where, judging from the above argument, one would expect (owing to the closeness of the atomic weights) a stability, show that Beketoff's addition to the mechanical theory of chemical phenomena is still far from sufficient for explaining the true relations of affinities. Nevertheless, in his mode of explaining the relative stabilities of compounds, we find an exceedingly interesting treatment of questions of primary importance. Without such efforts it would be impossible to generalise the complex data of experimental knowledge.

Fluoride of silver, AgF, is obtained by dissolving Ag_2O or Ag_2CO_3 in hydrofluoric acid. It differs from the other halogen salts of silver in being soluble in water (1 part of salt in 0·55 of water). It crystallises from its solution in prisms, $AgFH_2O$ (Marignac), or $AgF2H_2O$

substance be added to the alkali the chloride can easily be reduced to metallic silver, the silver oxide being reduced in the oxidation of the organic substance. Iron, zinc, and many other metals reduce silver chloride in the presence of water. Cuprous and mercurous chlorides and many organic substances are also able to reduce the silver from chloride of silver. This shows the rather easy decomposability of the halogen compounds of silver. Silver iodide is much more stable in this respect than the chloride. The same is also observed with respect to the *action of light* upon moist AgCl. White silver chloride soon acquires a violet colour when exposed to the action of light, and especially under the direct action of the sun's rays. After being acted upon by light it is no longer entirely soluble in ammonia, but leaves metallic silver undissolved, from which it might be assumed that the action of light consisted in the decomposition of the silver chloride into chlorine and metallic silver and in fact the silver chloride becomes in time darker and darker. Silver bromide and iodide are much more slowly acted on by light, and, according to certain observations, when pure they are even quite unacted on; at least they do not change in weight,[24 bis] so that if they are acted on by light, the change they undergo must be one of a change in the structure of their parts and not of decomposition, as it is in silver chloride. The silver chloride under the action of light changes in weight, which indicates the formation of a volatile product, and the deposition of metallic silver on dissolving in ammonia shows the loss of chlorine. The change does actually occur under the action of light, but the decomposition does not go as far as into chlorine and silver, but only to the formation of a subchloride of silver, Ag_2Cl, which is of a brown colour and is easily decomposed into metallic silver and silver chloride, $Ag_2Cl = AgCl + Ag$. This change of the chemical composition and structure of the halogen salts of silver under the action of light forms the basis of *photography*, because the halogen compounds of silver, after having been exposed to light, give a precipitate of finely-divided silver, of a black colour, when treated with reducing agents.[25]

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solution of Ag_2F, obtained *polyfluoride of silver*, Ag_2F, which is decomposed by water into $AgF + Ag$. It is also formed by the action of a strong solution of AgF upon finely-divided (precipitated) silver.

[24 bis] The changes brought about by the action of light necessitate distinguishing the photo-salts of silver.

[25] In photography these are called 'developers.' The most common developers are: solutions of ferrous sulphate, pyrogallol, ferrous oxalate, hydroxylamine, potassium sulphite, hydroquinone (the last acts particularly well and is very convenient to use), &c. The chemical processes of photography are of great practical and theoretical interest; but it would be impossible in this work to enter into this special branch of chemistry, which has as

The insolubility of the halogen compounds of silver forms the basis of many methods used in practical chemistry. Thus by means of this reaction it is possible to obtain salts of other acids from a halogen salt of a given metal, for instance, $RCl_2 + 2AgNO_3 = R(NO_3)_2 + 2AgCl$. The formation of the halogen compounds of silver is very frequently used in the investigation of organic substances; for example, if any product of metalepsis containing iodine or chlorine be heated with a silver salt or silver oxide, the silver combines with the halogen and gives a halogen salt, whilst the elements previously combined with the silver replace the halogen. For instance, ethylene dibromide, $C_2H_4Br_2$, is transformed into ethylene diacetate, $C_2H_4(C_2H_3O_2)_2$, and silver

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to consider certain aspects of this subject which are of a purely chemical interest, and especially the facts concerning *subchloride of silver*, Ag_2Cl (*see* Note 19), and the photo-salts (Note 28). There is no doubt that under the action of light, AgCl becomes darker in colour, decreases in weight, and probably forms a mixture of AgCl, Ag_2Cl, and Ag. But the isolation of the subchloride has only been recently accomplished by Güntz by means of the Ag_2F, discovered by him (*see* Note 24). Many chemists (and among them Hodgkinson) assumed that an oxychloride of silver was formed by the decomposition of AgCl under the action of light. Carey Lea's (1889) and A. Richardson's (1891) experiments showed that the product formed does not, however, contain any oxygen at all, and the change in colour produced by the action of light upon AgCl is most probably due to the formation of Ag_2Cl. This substance was isolated by Güntz (1891) by passing HCl over crystals of Ag_2F. He also obtained Ag_2I in a similar manner by passing HI, and Ag_2S by passing H_2S over Ag_2F. Ag_2Cl is best prepared by the action of phosphorus trichloride upon Ag_2F. At the temperature of its formation Ag_2Cl has an easily changeable tint, with shades of violet red to violet black. Under the action of light a similar (isomeric) substance is obtained, which splits up into AgCl + Ag when heated. With potassium cyanide Ag_2Cl gives $Ag + AgCN + KCl$, whence it is possible to calculate the heat of formation of Ag_2Cl; it $= 29·7$, whilst the heat of formation of AgCl $= 29·2$—*i.e.* the reaction $2AgCl = Ag_2Cl + Cl$ corresponds to an absorption of 28·7 major calories. If we admit the formation of such a compound by the action of light, it is evident that the energy of the light is consumed in the above reaction. Carey Lea (1892) subjected AgCl, AgBr, and AgI to a pressure (of course in the dark) of 3,000 atmospheres, and to trituration with water in a mortar, and observed a change of colour indicating incipient decomposition, which is facilitated under the action of light by the molecular currents set up (Lermontoff, Egoroff). The change of colour of the halogen salts of silver under the action of light, and their faculty of subsequently giving a visible photographic image under the action of 'developers,' must now be regarded as connected with the decomposition of AgX, leading to the formation of Ag_2X, and the different tinted photo-salts must be considered as systems containing such Ag_2X's. Carey Lea obtained photo-salts of this kind not only by the action of light but also in many other ways, which we will enumerate to prove that they contain the products of an incomplete combination of Ag with the halogens, (for the salts Ag_2X must be regarded as such). The photo-salts have been obtained (1) by the imperfect chlorination of silver; (2) by the incomplete decomposition of Ag_2O or Ag_2CO_3 by alternately heating and treating with a halogen acid; (3) by the action of nitric acid or $Na_2S_2O_3$ upon Ag_2Cl; (4) by mixing a solution of $AgNO_3$ with the hydrates of FeO, MnO and CrO, and precipitating by HCl; (5) by the action of HCl upon the product obtained by the reduction of citrate of silver in hydrogen (Note 19), and (6) by the action of milk sugar upon $AgNO_3$ together with soda and afterwards acidulating with HCl. All these reactions should lead to the formation of products of imperfect combination with the halogens and give photo-salts of a similar diversity of colour to those produced bromide by heating it with silver acetate, $2C_2H_3O_2Ag$. The insolubility of the halogen compounds of silver is still more frequently taken advantage of in determining the amount of silver and halogen in a given solution. If it is required, for instance, to determine the quantity of chlorine present in the form of a metallic chloride in a given solution, a solution of silver nitrate is added to it so long as it gives a precipitate. On *shaking or stirring* the liquid, the silver chloride easily settles in the form of heavy flakes. It is possible in this way to precipitate the whole of the chlorine from a solution, without adding an excess of silver nitrate, since it can be easily seen whether the addition of a fresh quantity of silver nitrate produces a precipitate in the clear liquid. In this manner it is possible to add to a solution containing chlorine, as much silver as is required for its entire precipitation, and to calculate the amount of chlorine previously in solution from the amount of the solution of silver nitrate consumed, if the quantity of silver nitrate in this solution has been previously determined.[25 bis] The atomic proportions and preliminary experiments with a pure salt—for example, with sodium chloride—will give the amount of chlorine from the quantity of silver nitrate. Details of these methods will be found in works on analytical chemistry.[25 tri]

[25 bis] In order to determine when the reaction is at an end, a few drops of a solution of K_2CrO_4 are added to the solution of the chloride. Before all the chlorine is precipitated as AgCl, the precipitate (after shaking) is white (since Ag_2CrO_4 with 2RCl gives 2AgCl); but when all the chlorine is thrown down Ag_2CrO_4 is formed, which colours the precipitate reddish-brown. In order to obtain accurate results the liquid should be neutral to litmus.

[25 tri] *Silver cyanide*, AgCN, is closely analogous to the haloid salts of silver. It is obtained, in similar manner to silver chloride, by the addition of potassium cyanide to silver nitrate. A white precipitate is then formed, which is almost insoluble in boiling water. It is also, like silver chloride, insoluble in dilute acids. However, it is dissolved when heated with nitric acid, and both hydriodic and hydrochloric acids act on it, converting it into silver chloride and iodide. Alkalis, however, do not act on silver cyanide, although they act on the other haloid salts of silver. Ammonia and solutions of the cyanides of the alkali metals dissolve silver cyanide, as they do the chloride. In the latter case double cyanides are formed—for example, $KAgC_2N_2$. This salt is obtained in a crystalline state on evaporating a solution of silver cyanide in potassium cyanide. It is much more stable than silver cyanide itself. It has a neutral reaction, does not change in the air, and does not smell of hydrocyanic acid. Many acids, in acting on a solution of this double salt, precipitate the insoluble silver cyanide. Metallic silver dissolves in a solution of potassium cyanide in the presence of air, with formation of the same double salt and potassium hydroxide, and when silver chloride dissolves in potassium cyanide it forms potassium chloride, besides the salt $KAgC_2N_2$. This double salt of silver is used in silver plating. For this purpose potassium cyanide is added to its solution, as otherwise silver cyanide, and not metallic silver, is deposited by the electric current. If two electrodes—one positive (silver) and the other negative (copper)—be immersed in such a solution, silver will be deposited upon the latter, and the silver of the positive electrode will be dissolved by the liquid, which will thus preserve the same amount of metal in solution as it originally contained. If instead of the

[illegible] These [illegible] have led to the [illegible] of the ordinary [illegible] and other chemicals, and are [illegible] and we will therefore describe them [illegible]. As calcium chloride is the chloride most generally used for the precipitation of silver, since it can most easily be obtained in a pure state, we will here give the [illegible] made by [illegible] for [illegible] of [illegible] and [illegible]

[illegible] 14 to 21 parts of [illegible] and [illegible] a [illegible] of [illegible] potassium [illegible] the [illegible] of silver [illegible] a [illegible] coating of silver, but if [illegible] the same [illegible] gives a brighter coating.

Silver plating in the wet way [illegible] employed [illegible] the [illegible] of dry [illegible] this process, which [illegible] the [illegible] of [illegible] silver [illegible] made by [illegible] of copper. The copper [illegible] and the silver [illegible] upon the copper. [illegible] a solution of silver chloride in [illegible] a coating of silver [illegible] of copper [illegible] It is best for this purpose to make paste [illegible]. This is prepared by [illegible] a solution of silver [illegible] with [illegible] of [illegible], and [illegible] a [illegible] of [illegible] and then [illegible] The [illegible] copper [illegible]

[illegible] plating [illegible] for [illegible] and [illegible] a [illegible] which is [illegible] than the ordinary [illegible] in the [illegible] of the [illegible] For [illegible] of silvered glass, which has first been ground and polished [illegible]. The silvering of glass is based on the fact that silver which is [illegible] and [illegible] upon [illegible] a [illegible] of [illegible]

[illegible] of [illegible] and the [illegible] as a brilliant, bright coating. The [illegible] is [illegible] and [illegible] sugar, and [illegible] &c.

chloride, he took pure rock salt, containing only a small
magnesia and calcium compounds and a small amount of
salts. This salt was dissolved in water, and the magnes
precipitated by boiling. The solution was separated
boiling, and the mother liquor containing the magnesium
off. Alcohol of 85 per cent strength was [illegible]
to the concentrated salt [illegible] precipitate [illegible] the
quantity [illegible] of the salt [illegible]. The precipitated salt
[illegible] and platinum chloride, was then
solution of pure ammonium chloride in order to remove
the excess. After this precipitation, the solution was evap
platinum retort, and then separate portions of the pur
chloride were collected as they crystallized. The same
pared from sodium sulphate, tartrate, nitrate, and from
chloride, in which he [illegible] prepared by
and in [illegible] and in these cases [illegible]
chloride thus prepared were purified and investigated in
silver. After being dried, weighed quantities of sil
of sodium chloride were dissolved in water and mixed wi
in nitric acid of a weighed quantity of perfectly pure
slightly greater quantity of silver was taken than would
for the precipitation of the sodium chloride, and when
ing [illegible] the [illegible] solution, the silver chloride had
amount of silver remaining in solution was determined
solution of sodium chloride of known strength. The
sodium chloride was added as long as it formed a precipit
number then determined how many parts of sodium ch
equal to 100 parts by weight of silver. The result of
tions was that for the entire precipitation of 100 par
from 54.2060 to 54.2081 parts of sodium chloride were
difference is so inconsiderable that it has no perceptib
on the [illegible] calculations. The mean of ten expe
that [illegible] parts of silver react with [illegible] parts of sod
[illegible] the ratio between the
[illegible] necessary to [illegible] the quantity of chlori
in [illegible] parts of sodium chloride, or, what is the same thing
of chlorine which combines with 100 parts of silver.
then made a series of observations on the quantity of
obtained from 100 parts of silver. Four syntheses were
[illegible]. The first synthesis consisted in the

Accurate experiments, and more especially the *researches of Stas* at Brussels, show the proportion in which silver reacts with metallic chlorides. These researches have led to the determination of the *combining weights* of silver, sodium, potassium, chlorine, bromine, iodine, and other elements, and are distinguished for their model exactitude, and we will therefore describe them in some detail. As sodium chloride is the chloride most generally used for the precipitation of silver, since it can most easily be obtained in a pure state, we will here cite the quantitative observations made by Stas for showing the co-relation between the quantities of chloride of sodium and silver which react together. In order to obtain perfectly pure sodium

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will be deposited in an even coating; this, indeed, forms the mode of *silver plating by the wet method*, which is most often used in practice. A solution of one part of silver nitrate in 30 to 50 parts of water, and mixed with a sufficient quantity of a solution of potassium cyanide to redissolve the precipitate of silver cyanide formed, gives a dull coating of silver, but if twice as much water be used the same mixture gives a bright coating.

Silver plating in the wet way has now replaced to a considerable extent the old process of *dry silvering*, because this process, which consists in dissolving silver in mercury and applying the amalgam to the surface of the objects, and then vaporising the mercury, offers the great disadvantage of the poisonous mercury fumes. Besides these, there is another method of silver plating, based on the direct displacement of silver from its salts by other metals—for example, by copper. The copper reduces the silver from its compounds, and the silver separated is deposited upon the copper. Thus a solution of silver chloride in sodium thiosulphate deposits a coating of silver upon a strip of copper immersed in it. It is best for this purpose to take pure *silver sulphite*. This is prepared by mixing a solution of silver nitrate with an excess of ammonia, and adding a saturated solution of sodium sulphite and then alcohol, which precipitates silver sulphite from the solution. The latter and its solutions are very easily decomposed by copper. Metallic iron produces the same decomposition, and iron and steel articles may be very readily silver-plated by means of the thiosulphate solution of silver chloride. Indeed, copper and similar metals may even be silver-plated by means of silver chloride; if the chloride of silver, with a small amount of acid, be rubbed upon the surface of the copper, the latter becomes covered with a coating of silver, which it has reduced.

Silver plating is not only applicable to metallic objects, but also to glass, china, &c. Glass is silvered for various purposes—for example, glass globes silvered internally are used for ornamentation, and have a mirrored surface. Common looking-glass silvered upon one side forms a mirror which is better than the ordinary mercury mirrors, owing to the truer colours of the image due to the whiteness of the silver. For optical instruments—for example, telescopes—concave mirrors are now made of silvered glass, which has first been ground and polished into the required form. The *silvering of glass* is based on the fact that silver which is reduced from certain solutions deposits itself uniformly in a perfectly homogeneous and continuous but very thin layer, forming a bright reflecting surface. Certain organic substances have the property of reducing silver in this form. The best known among these are certain aldehydes—for instance, ordinary acetaldehyde, C_2H_4O, which easily oxidises in the air and forms acetic acid, $C_2H_4O_2$. This oxidation also easily takes place at the expense of silver oxide, when a certain amount of ammonia is added to the mixture. The oxide of silver gives up its oxygen to the aldehyde, and the silver reduced from it is deposited in a metallic state in a uniform bright coating. The same action is produced by certain saccharine substances and chloride, he took pure rock salt, containing only a small quantity of magnesium and calcium compounds and a small amount of potassium salts. This salt was dissolved in water, and the saturated solution evaporated by boiling. The sodium chloride separated out during the boiling, and the mother liquor containing the impurities was poured off. Alcohol of 65 p.c. strength and platinic chloride were added to the resultant salt, in order to precipitate all the potassium and a certain part of the sodium salts. The resultant alcoholic solution, containing the sodium and platinum chlorides, was then mixed with a solution of pure ammonium chloride in order to remove the platinic chloride. After this precipitation, the solution was evaporated in a platinum retort, and then separate portions of this purified sodium chloride were collected as they crystallised. The same salt was prepared from sodium sulphate, tartrate, nitrate, and from the platinochloride, in order to have sodium chloride prepared by different methods and from different sources, and in this manner ten samples of sodium chloride thus prepared were purified and investigated in their relation to silver. After being dried, weighed quantities of all ten samples of sodium chloride were dissolved in water and mixed with a solution in nitric acid of a weighed quantity of perfectly pure silver. A slightly greater quantity of silver was taken than would be required for the decomposition of the sodium chloride, and when, after pouring in all the silver solution, the silver chloride had settled, the amount of silver remaining in excess was determined by means of a solution of sodium chloride of known strength. This solution of sodium chloride was added so long as it formed a precipitate. In this manner Stas determined how many parts of sodium chloride correspond to 100 parts by weight of silver. The result of ten determinations was that for the entire precipitation of 100 parts of silver, from 54·2060 to 54·2093 parts of sodium chloride were required. The difference is so inconsiderable that it has no perceptible influence on the subsequent calculations. The mean of ten experiments was that 100 parts of silver react with 54·2078 parts of sodium chloride. In order to learn from this the relation between the chlorine and silver, it was necessary to determine the quantity of chlorine contained in 54·2078 parts of sodium chloride, or, what is the same thing, the quantity of chlorine which combines with 100 parts of silver. For this purpose Stas made a series of observations on the quantity of silver chloride obtained from 100 parts of silver. Four syntheses were made by him for this purpose. The first synthesis consisted in the formation of silver chloride by the action of chlorine on silver at a red heat. This experiment showed that 100 parts of silver give 132·841, 132·843 and

132·843 of silver chloride. The second method consisted in dissolving a given quantity of silver in nitric acid and precipitating it by means of gaseous hydrochloric acid passed over the surface of the liquid; the resultant mass was evaporated in the dark to drive off the nitric acid and excess of hydrochloric acid, and the remaining silver chloride was fused first in an atmosphere of hydrochloric acid gas and then in air. In this process the silver chloride was not washed, and therefore there could be no loss from solution. Two experiments made by this method showed that 100 parts of silver give 132·849 and 132·846 parts of silver chloride. A third series of determinations was also made by precipitating a solution of silver nitrate with a certain excess of gaseous hydrochloric acid. The amount of silver chloride obtained was altogether 132·848. Lastly, a fourth determination was made by precipitating dissolved silver with a solution of ammonium chloride, when it was found that a considerable amount of silver (0·3175) had passed into solution in the washing; for 100 parts of silver there was obtained altogether 132·8417 of silver chloride. Thus from the mean of seven determinations it appears that 100 parts of silver give 132·8445 parts of silver chloride—that is, that 32·8445 parts of chlorine are able to combine with 100 parts of silver and with that quantity of sodium which is contained in 54·2078 parts of sodium chloride. These observations show that 32·8445 parts of chlorine combine with 100 parts of silver and with 21·3633 parts of sodium. From these figures expressing the relation between the combining weights of chlorine, silver, and sodium, it would be possible to determine their atomic weights—that is, the combining quantity of these elements with respect to one part by weight of hydrogen or 16 parts of oxygen, if there existed a series of similarly accurate determinations for the reactions between hydrogen or oxygen and one of these elements—chlorine, sodium, or silver. If we determine the quantity of silver chloride which is obtained from silver chlorate, $AgClO_3$, we shall know the relation between the combining weights of silver chloride and oxygen, so that, taking the quantity of oxygen as a constant magnitude, we can learn from this reaction the combining weight of silver chloride, and from the preceding numbers the combining weights of chlorine and silver. For this purpose it was first necessary to obtain pure silver chlorate. This Stas did by acting on silver oxide or carbonate, suspended in water, with gaseous chlorine.[26]

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[26] The phenomenon which then takes place is described by Stas as follows, in a manner which is perfect in its clearness and accuracy: if silver oxide or carbonate be suspended

The decomposition of the silver chlorate thus obtained was accomplished by the action of a solution of sulphurous anhydride on it. The salt was first fused by carefully heating it at 243°. The solution of sulphurous anhydride used was one saturated at 0°. Sulphurous anhydride in dilute solutions is oxidised at the expense of silver chlorate, even at low temperatures, with great ease if the liquid be continually shaken, sulphuric acid and silver chloride being formed: $AgClO_3 + 3SO_2 + 3H_2O = AgCl + 3H_2SO_4$. After decomposition, the resultant liquid was evaporated, and the residue of silver chloride weighed. Thus the process consisted in taking a known weight of silver chlorate, converting it into silver chloride, and determining the weight of the latter. The analysis conducted in this manner gave the following results, which, like the preceding, designate the weight in a vacuum calculated from the weights obtained in air: In the first experiment it appeared that 138·7890 grams of silver chlorate gave 103·9795 parts of silver chloride, and in the second experiment

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is converted into chloride, just as is the case with oxide or carbonate of mercury, and the water then contains, besides the excess of chlorine, only pure hypochlorous acid without the least trace of chloric or chlorous acid. If a stream of chlorine be passed into water containing *an excess of silver oxide* or silver carbonate while the liquid is continually agitated, the reaction is the same as the preceding; silver chloride and hypochlorous acid are formed. But this acid does not long remain in a free state: it gradually acts on the silver oxide and gives silver hypochlorite, *i.e.* $AgClO$. If, after some time, the current of chlorine be stopped but the shaking continued, the liquid loses its characteristic odour of hypochlorous acid, while preserving its energetic decolourising property, because the silver hypochlorite which is formed is easily soluble in water. In the presence of an excess of silver oxide this salt can be kept for several days without decomposition, but it is exceedingly unstable when no excess of silver oxide or carbonate is present. So long as the solution of silver hypochlorite is shaken up with the silver oxide, it preserves its transparency and bleaching property, but directly it is allowed to stand, and the silver oxide settles, it becomes rapidly cloudy and deposits large flakes of silver chloride, so that the black silver oxide which had settled becomes covered with the white precipitate. The liquid then loses its bleaching properties and contains silver chlorate, *i.e.* $AgClO_3$, in solution, which has a slightly alkaline reaction, owing to the presence of a small amount of dissolved oxide. In this manner the reactions which are consecutively accomplished may be expressed by the equations:

$$6Cl_2 + 3Ag_2O + 3H_2O = 6AgCl + 6HClO; \qquad 6HClO + 3Ag_2O = 3H_2O + 6AgClO;$$
$$6AgClO = 4AgCl + 2AgClO_3.$$

Hence, Stas gives the following method for the preparation of silver chlorate: A slow current of chlorine is caused to act on oxide of silver, suspended in water which is kept in a state of continual agitation. The shaking is continued after the supply of chlorine has been stopped, in order that the free hypochlorous acid should pass into silver hypochlorite, and the resultant solution of the hypochlorite is drawn off from the sediment of the excess of silver oxide. This solution decomposes spontaneously into silver chloride and chlorate. The pure silver chlorate, $AgClO_3$, does not change under the action of light. The salt is prepared for further use by drying it in dry air at 150°. It is necessary during drying to prevent the access of any organic matter; this is done by that 259·5287 grams of chlorate gave 194·44515 grams of silver chloride, and after fusion 194·4435 grams. The mean result of both experiments, converted into percentages, shows that 100 parts of silver chlorate contain 74·9205 of silver chloride and 25·0795 parts of oxygen. From this it is possible to calculate the combining weight of silver chloride, because in the decomposition of silver chlorate there are obtained three atoms of oxygen and one molecule of silver chloride: $AgClO_3 = AgCl + 3O$. Taking the weight of an atom of oxygen to be 16, we find from the mean result that the equivalent weight of silver chloride is equal to 143·395. Thus if $O=16$, $AgCl=143·395$, and as the preceding experiments show that silver chloride contains 32·8445 parts of chlorine per 100 parts of silver, the weight of the atom of silver[26 bis] must be 107·94 and that of chlorine 35·45 The weight of the atom of sodium is determined from the fact that 21·3633 parts of sodium chloride combine with 32·8445 parts of chlorine; consequently $Na=23·05$. This conclusion, arrived at by the analysis of silver chlorate, was verified by means of the analysis of potassium chlorate by decomposing it by heat and determining the weight of the potassium chloride formed, and also by effecting the same decomposition by igniting the chlorate in a stream of hydrochloric acid. The combining weight of potassium chloride was thus determined, and another series of determinations confirmed the relation between chlorine, potassium, and silver, in the same manner as the relation between sodium, chlorine, and silver was determined above. Consequently, the combining weights of sodium, chlorine, and potassium could be deduced by combining these data with the analysis of silver chlorate and the synthesis of silver chloride. The agreement between the results showed that the determinations made by the last method were perfectly correct, and did not depend in any considerable degree on the methods which were employed in the preceding determinations, as the combining weights of chlorine and silver obtained were the same as before. There was naturally a difference, but so small a one that it undoubtedly depended on the errors incidental to every process of weighing and experiment. The atomic weight of silver was also determined by Stas by means of the synthesis of silver sulphide and the analysis of silver sulphate. The combining weight obtained by this method was 107·920. The synthesis of silver iodide and the analysis of silver iodate gave the figure 107·928. The

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[26 bis] The results given by Stas' determinations have recently been recalculated and certain corrections have been introduced. We give in the context the average results of van der Plaat's and Thomsen's calculations, as well as in Table III. neglecting the

synthesis of silver bromide with the analysis of silver bromate gave the figure 107·921. The synthesis of silver chloride and the analysis of silver chlorate gave a mean result of 107·937. Hence there is no doubt that the combining weight of silver is at least as much as 107·9—greater than 107·90 and less than 107·95, and probably equal to the mean=107·92. Stas determined the combining weights of many other elements in this manner, such as lithium, potassium, sodium, bromine, chlorine, iodine, and also nitrogen, for the determination of the amount of silver nitrate obtained from a given amount of silver gives directly the combining weight of nitrogen. Taking that of oxygen as 16, he obtained the following combining weights for these elements: nitrogen 14·04, silver 107·93, chlorine 35·46, bromine 79·95, iodine 126·85, lithium 7·02, sodium 23·04, potassium 39·15. These figures differ slightly from those which are usually employed in chemical investigations. They must be regarded as the result of the best observations, whilst the figures usually used in practical chemistry are only approximate—are, so to speak, round numbers for the atomic weights which differ so little from the exact figures (for instance, for Ag 108 instead of 107·92, for Na 23 instead of 23·04) that in ordinary determinations and calculations the difference falls within the limits of experimental error inseparable from such determinations.

The exhaustive investigations conducted by Stas on the atomic weights of the above-named elements have great significance in the solution of the problem as to whether the atomic weights of the elements can be expressed in whole numbers if the unit taken be the atomic weight of hydrogen. Prout, at the beginning of this century, stated that this was the case, and held that the atomic weights of the elements are multiples of the atomic weight of hydrogen. The subsequent determinations of Berzelius, Penny, Marchand, Marignac, Dumas, and more especially of Stas, proved this conclusion to be untenable; since a whole series of elements proved to have fractional atomic weights—for example, chlorine, about 35·5. On account of this, Marignac and Dumas stated that the atomic weights of the elements are expressed in relation to hydrogen, either by whole numbers or by numbers with simple fractions of the magnitudes $\frac{1}{2}$ and $\frac{1}{4}$. But Stas's researches refute this supposition also. Even between the combining weight of hydrogen and oxygen, there is not, so far as is yet known, that simple relation which is required by *Prout's hypothesis*,[27]

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[27] This hypothesis, for the establishment or refutation of which so many researches have been made, is exceedingly important, and fully deserves the attention which has

i.e., taking O = 16, the atomic weight of hydrogen is equal not to 1 but to a greater number somewhere between 1·002 and 1·008 or mean·

be expressed in whole numbers with reference to hydrogen, or if they at least proved to be commensurable with one another, then it could be affirmed with confidence that the elements, with all their diversity, were formed of one material condensed or grouped in various manners into the stable, and, under known conditions, undecomposable groups which we call the atoms of the elements. At first it was supposed that all the elements were nothing else but condensed hydrogen, but when it appeared that the atomic weights of the elements could not be expressed in whole numbers in relation to hydrogen, it was still possible to imagine the existence of a certain material from which both hydrogen and all the other elements were formed. If it should transpire that four atoms of this material form an atom of hydrogen, then the atom of chlorine would present itself as consisting of 142 atoms of this substance, the weight of whose atom would be equal to 0·25. But in this case the atoms of all the elements should be expressed in whole numbers with respect to the weight of the atom of this original material. Let us suppose that the atomic weight of this material is equal to unity, then all the atomic weights should be expressible in whole numbers relatively to this unit. Thus the atom of one element, let us suppose, would weigh m, and of another n, but, as both m and n must be whole numbers, it follows that the atomic weights of all the elements would be commensurable. But it is sufficient to glance over the results obtained by Stas, and to be assured of their accuracy, especially for silver, in order to entirely destroy, or at least strongly undermine, this attractive hypothesis. We must therefore refuse our assent to the doctrine of the building up from a single substance of the elements known to us. This hypothesis is not supported either by any known transformation (for one element has never been converted into another element), or by the commensurability of the atomic weights of the elements. Although the hypothesis of the formation of all the elements from a single substance (for which Crookes has suggested the name protyle) is most attractive in its comprehensiveness, it can neither be denied nor accepted for want of sufficient data. Marignac endeavoured, however, to overcome Stas's conclusions as to the incommensurability of the atomic weights by supposing that in his, as in the determinations of all other observers, there were unperceived errors which were quite independent of the mode of observation—for example, silver nitrate might be supposed to be an unstable substance which changes, under the heatings, evaporations, and other processes to which it is subjected in the reactions for the determination of the combining weight of silver. It might be supposed, for instance, that silver nitrate contains some impurity which cannot be removed by any means; it might also be supposed that a portion of the elements of the nitric acid are disengaged in the evaporation of the solution of silver nitrate (owing to the decomposing action of water), and in its fusion, and that we have not to deal with normal silver nitrate, but with a slightly basic salt, or perhaps an excess of nitric acid which cannot be removed from the salt. In this case the observed combining weight will not refer to an actually definite chemical compound, but to some mixture for which there does not exist any perfectly exact combining relations. Marignac upholds this proposition by the fact that the conclusions of Stas and other observers respecting the combining weights determined with the greatest exactitude very nearly agree with the proposition of the commensurability of the atomic weights—for example, the combining weight of silver was shown to be equal to 107·93, so that it only differs by 0·08 from the whole number 108, which is generally accepted for silver. The combining weight of iodine proved to be equal to 126·85—that is, it differs from 127 by 0·15. The combining weights of sodium, nitrogen, bromine, chlorine, and lithium are still nearer to the whole or round numbers which are generally accepted. But Marignac's proposition will hardly bear criticism. Indeed if we express the combining weights of the elements determined by Stas in relation to hydrogen, the approximation of these weights to whole numbers disappears, because one part of hydrogen in reality does not combine with 16 parts of oxygen, but with 15·92 parts, and therefore we shall obtain, taking H = 1, not the above-

1 005. Such a conclusion arrived at by direct experiment cannot but be regarded as having greater weight than Prout's supposition (hypothesis) that the atomic weights of the elements are in multiple proportion to each other, which would give reason for surmising (but not asserting) a complexity of nature in the elements, and their common origin from a single primary material, and for expecting their mutual conversion into each other. All such ideas and hopes must

removed from whole numbers. Besides which, if Marignac's proposition were true the combining weight of silver determined by one method—*e.g.* by the analysis of silver chlorate combined with the synthesis of silver chloride—would not agree well with the combining weight determined by another method—*e.g.* by means of the analysis of silver iodate and the synthesis of silver iodide. If in one case a basic salt could be obtained, in the other case an acid salt might be obtained. Then the analysis of the acid salt would give different results from that of the basic salt. Thus Marignac's arguments cannot serve as a support for the vindication of Prout's hypothesis.

In conclusion, I think it will not be out of place to cite the following passage from a paper I read before the Chemical Society of London in 1889 (Appendix II.), referring to the hypothesis of the complexity of the elements recognised in chemistry, owing to the fact that many have endeavoured to apply the periodic law to the justification of this idea 'dating from a remote antiquity, when it was found convenient to admit the existence of many gods but only one matter.

'When we try to explain the origin of the idea of a unique primary matter, we easily trace that, in the absence of deductions from experiment, it derives its origin from the scientifically philosophical attempt at discovering some kind of unity in the immense diversity of individualities which we see around. In classical times such a tendency could only be satisfied by conceptions about the immaterial world. As to the material world, our ancestors were compelled to resort to some hypothesis, and they adopted the idea of unity in the formative material, because they were not able to evolve the conception of any other possible unity in order to connect the multifarious relations of matter. Responding to the same legitimate scientific tendency, natural science has discovered throughout the universe a unity of plan, a unity of forces, and a unity of matter; and the convincing conclusions of modern science compel every one to admit these kinds of unity. But while we admit unity in many things, we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere. It was said of old "Give us a fulcrum and it will become easy to displace the earth." So also we must say, "Give us something that is individualised, and the apparent diversity will be easily understood." Otherwise, how could unity result in a multitude

'After a long and painstaking research, natural science has discovered the individualities of the chemical elements, and therefore it is now capable, not only of analysing, but also of synthesising; it can understand and grasp generality and unity, as well as the individualised and multifarious. The general and universal, like time and space, like force and motion, vary uniformly. The uniform admit of interpolations, revealing every intermediate phase; but the multitudinous, the individualised—such as ourselves, or the chemical elements, or the members of a peculiar periodic function of the elements, or Dalton's multiple proportions—is characterised in another way. We see in it—side by side with a general connecting principle—leaps, breaks of continuity, points which escape from the analysis of the infinitely small—an absence of complete intermediate links. Chemistry has found an answer to the question as to the causes of multitudes, and while retaining the conception of many elements, all submitted to the discipline of a general law, it offers an escape from the Indian Nirvana—the absorption in the universal—replacing it by the individualised. However, the place for individuality is so limited by the all-grasping, all-powerful universal, that it is merely a point of support for the under-now, thanks more especially to Stas, be placed in a region void of any experimental support whatever, and therefore not subject to the discipline of the positive data of science.

Among the platinum metals ruthenium, rhodium, and palladium, by their atomic weights and properties, approach silver, just as iron and its analogues (cobalt and nickel) approach copper in all respects. *Gold* stands in exactly the same position in relation to the heavy platinum metals, osmium, iridium, and platinum, as copper and silver do to the two preceding series. The atomic weight of gold is nearly equal to their atomic weights;[28] it is dense like these metals. It also gives various grades of oxidation, which are feeble, both in a basic and an acid sense. Whilst near to osmium, iridium, and platinum, gold at the same time is able, like copper and silver, to form compounds which answer to the type RX—that is, oxides of the composition R_2O. Cuprous chloride, CuCl, silver chloride, AgCl, and aurous chloride, AuCl, are substances which are very much alike in their physical and chemical properties.[28 bis] They are insoluble in water, but dissolve in hydrochloric acid and ammonia, in potassium cyanide,

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[28] It might be expected from the periodic law and analogies with the series iron, cobalt, nickel, copper, zinc, that the atomic weights of the elements of the series osmium, iridium, platinum, gold, mercury, would rise in this order, and at the time of the establishment of the periodic law (1869), the determinations of Berzelius, Rose, and others gave the following values for the atomic weights: Os = 200, Ir = 197, Pt = 198, Au = 196, Hg = 200. The fulfilment of the expectations of the periodic law was given in the first place by the fresh determinations (Seubert, Dittmar, and Arthur) of the atomic weight of platinum, which proved to be nearly 196, if O = 16 (as Marignac, Brauner, and others propose); in the second place, by the fact that Seubert proved that the atomic weight of osmium is really less than that of platinum, and approximately Os = 191; and, in the third place, by the fact that after the researches of Krüss, Thorpe, and Laurie there was no doubt that the atomic weight of gold is greater than that of platinum namely, nearly 197.

[28 bis] In Chapter XXII., Note 40, we gave the thermal data for certain of the compounds of copper of the type CuX_2; we will now cite certain data for the cuprous compounds of the type CuX, which present an analogy to the corresponding compounds AgX and AuX, some of which were investigated by Thomsen in his classical work, 'Thermochemische Untersuchungen' (Vol. iii., 1883). The data are given in the same manner as in the above-mentioned note:

R =	Cu	Ag	Au
R + Cl	+ 33	+ 29	+ 6
R + Br	+ 25	+ 23	0
R + I	+ 16	+ 14	− 6
R + O	+ 41	+ 6	− ?

Thus we see in the first place that gold, which possesses a much smaller affinity than Ag, evolves far less heat than an equivalent amount of copper, giving the same compound, and in the second place that the combination of copper with one atom of oxygen disengages more heat than its combination with one atom of a halogen, whilst with silver the reverse is the case. This is connected with the fact that Cu_2O is more stable under the action

sodium thiosulphate, &c. Just as copper forms a link betwee
metals and zinc, and as silver unites the light platinum m
cadmium, so also gold presents a transition from the heavy
metals to mercury. Copper gives saline compounds of the t
and CuX_2, silver of the type AgX, whilst gold, besides com
the type AuX, very easily and most frequently forms those o
$AuCl_3$. The compounds of this type frequently pass into th
lower type, just as PtX_4 passes into PtX_2, and the same is
in the elements which, in their atomic weights, follow gold.
gives HgX_2 and HgX, thallium gives TlX_3 and TlX,
PbX_4 and PbX_2. On the other hand, gold in a qualitati
differs from silver and copper in the *extreme ease* with which a
pounds are *reduced to metal* by many means. This is not on
plished by many reducing agents, but also by the action of he
its chlorides and oxides lose their chlorine and oxygen whe
and, if the temperature be sufficiently high, these elements a
expelled and metallic gold alone remains. Its compounds,
act as oxidising agents.[29]

In nature gold occurs in the primary and chiefly in quart
and especially in quartz veins, as in the Urals (at Bere
Australia, and in California. The native gold is extracted
rocks by subjecting them to a mechanical treatment co
crushing and washing.[29 bis] Nature has already accomplishe

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[29] Heavy atoms and molecules, although they may present many points o
more easily isolated; thus $C_{10}H_{32}$, although, like C_2H_4, it combines with B
similar composition, yet reacts with much greater difficulty than C_2H_4, and in
bles gold; the heavy atoms and molecules are, so to say, inert, and already
themselves. Gold in its higher grade of oxidation, Au_2O_3, presents feeb
perties and weakly-developed acid properties, so that this oxide of gold, A
referred to the class of feeble acid oxides, like platinic oxide. This is not th
highest known oxides of copper and silver. But in the lower grade of oxid
oxide, Au_2O, gold, like silver and copper, presents basic properties, althou
not very pronounced. In this respect it stands very close in its propert
not in its types of combination (AuX and AuX_3), to platinum (PtX_2 and P
analogues.

As yet the general chemical characteristics of gold and its compounds h
fully investigated. This is partly due to the fact that very few researche
undertaken on the compounds of this metal, owing to its inaccessibility
in large quantities. As the atomic weight of gold is high (Au = 197), the p
its compounds requires that it should be taken in large quantities, whi
obstacle to its being fully studied. Hence the facts concerning the history
are rarely distinguished by that exactitude with which many facts have bee
concerning other elements more accessible, and long known in use.

[29 bis] Sonstadt (1872) showed that sea water, besides silver, always co
Munster (1892) showed that the water of the Norwegian fiords contains a
grams of gold per ton (or 5 milliardths)—*i.e.* a quantity deserving practical a
I think it may be already said that, considering the immeasurable amount

disintegration of the hard rocky matter containing gold.[30] These disintegrated rocks, washed by rain and other water, have formed gold-bearing deposits, which are known as *alluvial gold deposits.* Gold-bearing soil is sometimes met with on the surface and sometimes under

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bringing it into contact with substances capable of depositing gold upon their surface. The first efforts might be made upon the extraction of salt from sea water, and as the total amount of sea water may be taken as about 2,000,000,000,000,000,000 tons, it follows that it contains about 10,000 million tons of gold. The yearly production of gold is about 200 tons for the whole world, of which about one quarter is extracted in Russia. It is supposed that gold is dissolved in sea water owing to the presence of iodides, which, under the action of animal organisms, yield free iodine. It is thought (as Professor Konovaloff mentions in his work upon 'The Industries of the United States,' 1894) that iodine facilitates the solution of the gold, and the organic matter its precipitation. These facts and considerations to a certain extent explain the distribution of gold in veins or rock fissures, chiefly filled with quartz, because there is sufficient reason for supposing that these rocks once formed the ocean bottom. R. Dentrie, and subsequently Wilkinson, showed that organic matter—for instance, cork—and pyrites are able to precipitate gold from its solutions in that metallic form and state in which it occurs in quartz veins, where (especially in the deeper parts of vein deposits) gold is frequently found on the surface of pyrites, chiefly arsenical pyrites. Kazantseff (in Ekaterinburg, 1891) even supposes, from the distribution of the gold in these pyrites, that it occurred in solution as a compound of sulphide of gold and sulphide of arsenic when it penetrated into the veins. It is from such considerations that the origin of vein and pyritic gold is, at the present time, attributed to the reaction of solutions of this metal, the remains of which are seen in the gold still present in sea water.

[30] However, in recent times, especially since about 1870, when chlorine (either as a solution of the gas or as bleaching powder) and bromine began to be applied to the extraction of finely-divided gold from poor ores (previously roasted in order to drive off arsenic and sulphur, and oxidise the iron), the extraction of gold from quartz and pyrites, by the wet method, increases from year to year, and begins to equal the amount extracted from alluvial deposits. Since the nineties the *cyanide process* (Chapter XIII., Note 18 bis) has taken an important place among the wet methods for extracting gold from its ores. It consists in pouring a dilute solution of cyanide of potassium (about 500 parts of water and 1 to 4 parts of cyanide of potassium per 1,000 parts of ore, the amount of cyanide depending upon the richness of the ore) and a mixture of it with NaCN, (*see* Chapter XIII., Note 12) over the crushed ore (which need not be roasted, whilst roasting is indispensable in the chlorination process, as otherwise the chlorine is used up in oxidising the sulphur, arsenic, &c.) The gold is dissolved very rapidly even from pyrites, where it generally occurs on the surface in such fine and adherent particles that it either cannot be mechanically washed away, or, more frequently is carried away by the stream of water, and cannot be caught by mechanical means or by the mercury used for catching the gold in the sluices. Chlorination had already given the possibility of extracting the finest particles of gold; but the cyanide process enables such pyrites to be treated as could be scarcely worked by other means. The treatment of the crushed ore by the KCN is carried on in simple wooden vats (coated with paraffin or tar) with the greatest possible rapidity (in order that the KCN solution should not have time to change) by a method of systematic lixiviation, and is completed in 10 to 12 hours. The resultant solution of gold, containing $AuK(CN)_2$, is decomposed either with freshly-made zinc filings (but when the gold settles on the Zn, the cyanide solution reacts upon the Zn with the evolution of H_2 and formation of ZnH_2O_2) or by sodium amalgam prepared at the moment of reaction by the action of an electric current upon a solution of NaHO poured into a vessel partially immersed in mercury (the NaCN is renewed continually by this means). The silver in the ore passes

the upper soil, but more frequently along the banks of dri
courses and running streams. The sand of many rive
however, a very small amount of gold, which it is not
work; for example, that of the Alpine rivers contains 5 p
in 10,000,000 parts of sand. The richest gold deposits
Siberia, especially in the southern parts of the Government
the South Urals, Mexico, California, South Africa, an
and then the comparatively poorer alluvial deposits of ma
(Hungary, the Alps, and Spain in Europe). The extrac
gold from alluvial deposits is based on the principle of lev
earth is washed, while constantly agitated, by a strea
which carries away the lighter portion of the earth, and
coarser particles of the rock and heavier particles of the g
with certain substances which accompany it, in the washin
The extraction of this *washed* gold only necessitates me
pliances,[31] and it is not therefore surprising that gold wa
savages and in the most remote period of history. It some
in crystals belonging to the regular system, but in the maj

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[31] But the particles of gold are sometimes so small that a large amou
the washing. It is then profitable to have recourse to the extraction
KCN (Note 30).

In speaking of the extraction of gold the following remarks may
place:

In California advantage is taken of water supplied from high altitu
have a powerful head of water, with which the rocks are directly was
avoiding the greater portion of the mechanical labour required for the
these deposits.

The last residues of gold are sometimes extracted from sand by was
mercury, which dissolves the gold. The sand mixed with water is cause
contact with mercury during the washing. The mercury is then distille

Many sulphurous ores, even pyrites, contain a small amount of gold.
gold with bismuth, $BiAu_2$, tellurium, $AuTe_2$ (calverite), &c., have been
rarely.

Among the minerals which accompany gold, and from which the prese
be expected, we may mention white quartz, titanic and magnetic iron or
following, which are of rarer occurrence: zircon, topaz, garnet, and such
centrated gold washings first undergo a mechanical treatment, and th
obtained is treated for pure gold by various methods. If the gold contai
amount of foreign metals, especially lead and copper, it is sometimes cupe
so that the oxidisable metals may be absorbed by the cupel in the form
every case the gold is obtained together with silver, because the latter n
oxidised. Sometimes the gold is extracted by means of mercury, that is
tion (and the mercury subsequently driven off by distillation), or by s
lead (which is afterwards removed by oxidation) and processes like thos
the extraction of silver, because gold, like silver, does not oxidise, is di
and mercury, and is non-volatile. If copper or any other metal contai
employed as an anode, pure copper will be deposited upon the cathod
gold will remain at the anode as a slime. This method often amply r
cost of the process, since it gives, besides the gold, a pure electrolytic c

in nuggets or grains of greater or less magnitude. It always contains silver (from very small quantities up to 30 p.c., when it is called 'electrum') and certain other metals, among which lead and rhodium are sometimes found.

The separation of the silver from gold is generally carried on with great precision, as the presence of the silver in the gold does not increase its value for exchange, and it can be substituted by other less valuable metals, so that the extraction of the silver, as a precious metal, from its alloy with gold, is a profitable operation. This separation is conducted by different methods. Sometimes the argentiferous gold is melted in crucibles, together with a mixture of common salt and powdered bricks. The greater portion of the silver is thus converted into the chloride, which fuses and is absorbed by the slags, from which it may be extracted by the usual methods. The silver is also extracted from gold by treating it with boiling sulphuric acid, which does not act on the gold but dissolves the silver. But if the alloy does not contain a large proportion of silver it cannot be extracted by this method or at all events the separation will be imperfect, and therefore a fresh amount of silver is added (by fusion) to the gold, in such quantity that the alloy contains twice as much silver as gold. The silver which is added is preferably such as contains gold, which is very frequently the case. The alloy thus formed is poured in a thin stream into water, by which means it is obtained in a granulated form; it is then boiled with strong sulphuric acid, three parts of acid being used to one part of alloy. The sulphuric acid extracts all the silver without acting on the gold. It is best, however, to pour off the first portion of the acid, which has dissolved the silver, and then treat the residue of still imperfectly pure gold with a fresh quantity of sulphuric acid. The gold is thus obtained in the form of powder, which is washed with water until it is quite free from silver. The silver is precipitated from the solution by means of copper, so that cupric sulphate and metallic silver are obtained. This process is carried out in many countries, as in Russia, at the Government mints.

Gold is generally used alloyed with copper; since pure gold, like pure silver, is very soft, and therefore soon worn away. In assaying or determining the amount of pure gold in such an alloy it is usual to add silver to the gold in order to make up an alloy containing three parts of silver to one of gold (this is known as quartation because the alloy contains $\frac{1}{4}$ of gold), and the resultant alloy is treated with nitric acid. If the silver be not in excess over the gold, it is not all dissolved by the nitric acid, and this is the reason for the quartation. The amount of pure gold (assay) is determined by weighing the gold which remains after this treatment. English gold (= 22 carats) coinage is composed of an alloy containing 91·66 p.c. of gold, but for many articles gold is frequently used containing a larger amount of foreign metals.

Pure gold may be obtained from gold alloys by dissolving in aqua regia, and then adding ferrous sulphate to the solution or heating it with a solution of oxalic acid. These deoxidising agents reduce the gold, but not the other metals. The chlorine combined with the gold then acts like free chlorine. The gold, thus reduced, is precipitated as an exceedingly fine brown powder.[31 bis] It is then washed with water, and fused with nitre or borax. Pure gold reflects a yellow light, and in the form of very thin sheets (gold leaf), into which it can be hammered and rolled,[31 tri] it transmits a bluish-green light. The specific gravity of gold is about 19·5, the sp. gr. of gold coin is about 17·1. It fuses at 1090°—at a higher temperature than silver—and can be drawn into exceedingly fine wires or hammered into thin sheets. With its softness and ductility, gold is distinguished for its tenacity, and a gold wire two millimetres thick breaks only under a load of 68 kilograms. Gold vaporises even at a furnace heat, and imparts a greenish colour to a flame passing over it in a furnace. Gold alloys with copper almost without changing its volume.[32] In its chemical

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[31 bis] Schottländer (1893) obtained gold in a soluble colloid form (the solution is violet) by the action of a mixture of solutions of cerium acetate and NaHO upon a solution of $AuCl_3$. The gold separates out from such a solution in exactly the same manner as Ag does from the solution of colloid silver mentioned above. There always remains a certain amount of a higher oxide of cerium, CeO_2, in the solution—*i.e.* the gold is reduced by converting the cerium into a higher grade of oxidation. Besides which Krüss and Hofmann showed that sulphide of gold precipitated by the action of H_2S upon a solution of $AuKCy_2$ mixed with HCl easily passes into a colloid solution after being properly washed (like As_2S_3, CuS, &c., Chapter I., Note 57).

[31 tri] Gold-leaf is used for gilding wood (leather, cardboard, and suchlike, upon which it is glued by means of varnish, &c.), and is about 0·008 millimetre thick. It is obtained from thin sheets (weighing at first about ¼ grm. to a square inch), rolled between gold rollers, by gradually hammering them (in packets of a number at once) between sheets of moist (but not wet) parchment, and then, after cutting them into four pieces, between a specially prepared membrane, which, when at the right degree of moisture, does not tear or stick together under the blows of the hammer.

[32] The formation of the alloys Cu + Zn, Cu + Sn, Cu + Bi, Cu + Sb, Pb + Sb, Ag + Pb, Ag + Sn, Au + Zn, Au + Sn, &c., is accompanied by a contraction (and evolution of heat). The formation of the alloys Fe + Sb, Fe + Pb, Cu + Pb, Pb + Sn, Pb + Sn, Pb + Sb, Zn + Sb, Ag + Cu, Au + Cu, Au + Pb, takes place with a certain increase in volume. With regard to the alloys of gold, it may be mentioned that gold is only slightly dissolved by mercury (about 0·06 p.c., Dudley, 1890); the remaining portion forms a granular alloy, whose composition has not been definitely determined. Aluminium (and silicon) also have the capacity of forming alloys with gold. The presence of a small amount of aluminium lowers the melting point of gold considerably (Roberts-Austen, 1892); thus the addition of 4 p.c. of aluminium lowers it by 14°·28, the addition of 10 p.c.

aspect, gold presents, as is already seen from its general characteristics given above, an example of the so-called noble metals—*i.e.* it is incapable of being oxidised at any temperature, and its oxide is decomposed when calcined. Only chlorine and bromine combine directly with it at the ordinary temperature, but many other metals and non-metals combine with it at a red heat—for example, sulphur, phosphorus, and arsenic. Mercury dissolves it with great ease. It dissolves in potassium cyanide in the presence of air; a mixture of sulphuric acid with nitric acid dissolves it with the aid of heat, although in small quantity. It is also soluble in aqua regia and in selenic acid. Sulphuric, hydrochloric, nitric, and hydrofluoric acids and the caustic alkalis do not act on gold, but a mixture of hydrochloric acid with such oxidising agents as evolve chlorine naturally dissolves it like aqua regia.[32 bis]

As regards the compounds of gold, they belong, as was said above, to the types AuX_3 and AuX. *Auric chloride* or *gold trichloride*, $AuCl_3$, which is formed when gold is dissolved in aqua regia, belongs to the former and higher of these types. The solution of this substance in water has a yellow colour, and it may be obtained pure by evaporating the solution in aqua regia to dryness, but not to the point of decomposition. If the evaporation proceed to the point of crystallisation, a compound of gold chloride and hydrochloric acid, $AuHCl_4$, is obtained, like the allied compounds of platinum; but it easily parts with the acid and leaves auric chloride, which fuses into a red-brown liquid, and then solidifies to a crystalline mass. If dry chlorine be passed over gold in powder it forms a mixture of aurous and auric chlorides, but the aurous chloride is also decomposed by water into gold and auric chloride. Auric chloride crystallises from its solutions as $AuCl_3,2H_2O$, which easily loses water, and the dry chloride loses two-thirds of its chlorine at 185°, forming aurous chloride, whilst

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Al by 41°·7. The latter alloy is white. The alloy $AuAl_2$ has a characteristic purple colour, and its melting point is 32°·5 above that of gold, which shows it to be a definite compound of the two metals. The melting points of alloys richer in Al gradually fall to 660°—that is, below that of aluminium (665°).

Heycock and Neville (1892), in studying the triple alloys of Au, Cd, and Sn, observed a tendency in the gold to give compounds with Cd, and by sealing a mixture of Au and Cd in a tube, from which the air had been exhausted, and heating it, they obtained a grey crystalline brittle definite alloy AuCd.

[32 bis] Calderon (1892), at the request of some jewellers, investigated the cause of a peculiar alteration sometimes found on the surface of dead-gold articles, there appearing brownish and blackish spots, which widen and alter their form in course of time. He came to the conclusion that these spots are due to the appearance and development of peculiar micro-organisms (Aspergillus niger and Micrococcus cimbareus) on the gold, spores of which were found in abundance on the cotton-wool in which the gold articles had been kept.

above 300° the latter chloride also loses its chlorine and leaves metallic gold. Auric chloride is the usual form in which gold occurs in solutions, and in which its salts are used in the arts and for chemical purposes. It is soluble in water, alcohol, and ether. Light has a reducing action on these solutions, and after a time metallic gold is deposited upon the sides of vessels containing the solution. Hydrogen when nascent, and even in a gaseous form, reduces gold from this solution to a metallic state. The reduction is more conveniently and usually effected by ferrous sulphate, and in general by the action of ferrous salts.[33]

If a solution of potassium hydroxide be added to a solution of auric chloride, a precipitate is first formed, which re-dissolves in an excess of the alkali. On being evaporated under the receiver of an air-pump, this solution yields yellow crystals, which present the same composition as the double salts $AuMCl_4$, with the substitution of the chlorine by oxygen—that is to say, *potassium aurate*, $AuKO_2$, is formed in crystals containing $3H_2O$. The solution has a distinctly alkaline reaction. *Auric oxide*, Au_2O_3, separates when this alkaline solution is boiled with an excess of sulphuric acid. But it then still retains some alkali; however, it may be obtained in a pure state as a brown powder by dissolving in nitric acid and diluting with water. The brown powder decomposes below 250° into gold and oxygen. It is insoluble in water and in many acids, but it dissolves in alkalis, which shows the acid character of this oxide. An hydroxide, $Au(OH)_3$, may be obtained as a brown powder by adding magnesium oxide to a solution of auric chloride and treating the resultant precipitate of magnesium aurate with nitric acid. This hydroxide loses water at 100°. and gives auric oxide.[34]

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[33] Stannous chloride as a reducing agent also acts on auric chloride, and gives a red precipitate known as *purple of Cassius*. This substance, which probably contains a mixture or compound of aurous oxide and tin oxide, is used as a red pigment for china and glass. Oxalic acid, on heating, reduces metallic gold from its salts, and this property may be taken advantage of for separating it from its solutions. The oxidation which then takes place in the presence of water may be expressed by the following equation: $2AuCl_3 + 3C_2H_2O_4 = 2Au + 6HCl + 6CO_2$. Nearly all organic substances have a reducing action on gold, and solutions of gold leave a violet stain on the skin.

Auric chloride, like platinic chloride, is distinguished for its clearly-developed property of forming double salts. These double salts, as a rule, belong to the type $AuMCl_4$. The compound of auric chloride with hydrochloric acid mentioned above evidently belongs to the same type. The compounds $2KAuCl_4,5H_2O$, $NaAuCl_4,2H_2O$, $AuNH_4Cl_4,H_2O$, $Mg(AuCl_4)_2,2H_2O$, and the like are easily crystallised in well-formed crystals. Wells, Wheeler, and Penfield (1892) obtained $RbAuCl_4$ (reddish yellow) and $CsAuCl_4$ (golden yellow), and corresponding bromides (dark coloured). $AuBr_3$ is extremely like the chloride. Auric cyanide is obtained easily in the form of a double salt of potassium, $KAu(CN)_4$, by mixing saturated and hot solutions of potassium cyanide with auric chloride and then cooling.

[34] If ammonia be added to a solution of auric chloride, it forms a yellow precipitate

The starting-point of the compounds of the type AuX [35] is *gold monochloride* or *aurous chloride*, AuCl, which is formed, as mentioned above, by heating auric chloride at 185°. Aurous chloride forms a yellowish-white powder; this, when heated with water, is decomposed into metallic gold and auric chloride, which passes into solution: $3AuCl = AuCl_3 + 2Au$. This decomposition is accelerated by the action of light. Hence it is obvious that the compounds corresponding with aurous oxide are comparatively unstable. But this only refers to the simple compounds AuX; some of the complex compounds, on the contrary, form the most stable compounds of gold. Such, for example, is the cyanide of gold and potassium, $AuK(CN)_2$. It is formed, for instance, when finely-divided gold dissolves in the presence of air in a solution of potassium cyanide: $4KCN + 2Au + H_2O + O = 2KAu(CN)_2 + 2KHO$ (this reaction also proceeds with solid pieces of gold, although very slowly). The same compound is formed in solution when many compounds of gold are mixed with potassium cyanide, because if a higher compound of gold be taken, it is reduced

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of the so-called fulminating gold, which contains gold, chlorine, hydrogen, nitrogen, and oxygen, but its formula is not known with certainty. It is probably a sort of ammonio-metallic compound, $Au_2O_3,4NH_3$, or amide (like the mercury compound). This precipitate explodes at 140°, but when left in the presence of solutions containing ammonia it loses all its chlorine and becomes non-explosive. In this form the composition $Au_2O_3,2NH_3,H_2O$ is ascribed to it, but this is uncertain. Auric sulphide, Au_2S_3, is obtained by the action of hydrogen sulphide on a solution of auric chloride, and also directly by fusing sulphur with gold. It has an acid character, and therefore dissolves in sodium and ammonium sulphides.

[35] Many double salts of suboxide of gold belong to the type AuX—for instance, the cyanide corresponding to the type $AuKX_2$, like PtK_2X_4, with which we became acquainted in the last chapter. We will enumerate several of the representatives of this class of compounds. If auric chloride, $AuCl_3$, be mixed with a solution of sodium thiosulphate, the gold passes into a colourless solution, which deposits colourless crystals, containing a double thiosulphate of gold and sodium, which are easily soluble in water but are precipitated by alcohol. The composition of this salt is $Na_3Au(S_2O_3)_2,2H_2O$. If the sodium thiosulphate be represented as NaS_2O_3Na, the double salt in question will be $AuNa(S_2O_3Na)_2,2H_2O$, according to the type $AuNaX_2$. The solution of this colourless and easily crystallisable salt has a sweet taste, and the gold is not separated from it either by ferrous sulphate or oxalic acid. This salt, which is known as *Fordos and Gelis's salt*, is used in medicine and photography. In general, aurous oxide exhibits a distinct inclination to the formation of similar double salts, as we saw also with PtX_2—for example, it forms similar salts with sulphurous acid. Thus if a solution of sodium sulphite be gradually added to a solution of oxide of gold in sodium hydroxide, the precipitate at first formed re-dissolves to a colourless solution, which contains the double salt $Na_3Au(SO_3)_2 = AuNa(SO_3Na)_2$. The solution of this salt, when mixed with barium chloride, first forms a precipitate of barium sulphite, and then a red barium double salt which corresponds with the above sodium salt.

The oxygen compound of the type AuX, *aurous oxide*, Au_2O, is obtained as a greenish violet powder on mixing aurous chloride with potassium chloride in the cold. With hydrochloric acid this oxide gives gold and auric chloride, and when heated it easily splits up into oxygen and metallic gold.

by the potassium cyanide into aurous oxide, which dissolves in potassium cyanide and forms $KAu(CN)_2$. This substance is soluble in water, and gives a colourless solution, which can be kept for a long time, and is employed in electro-gilding—that is, for coating other metallic objects with a layer of gold, which is deposited if the object be connected with the negative pole of a battery and the positive pole consist of a gold plate. When an electric current is passed between them, the gold from the latter will dissolve, whilst a coating of gold from the solution will be deposited on the object.

APPENDIX I

AN ATTEMPT TO APPLY TO CHEMISTRY ONE OF THE PRINCIPLES OF NEWTON'S NATURAL PHILOSOPHY

BY PROFESSOR MENDELÉEFF

A LECTURE DELIVERED AT THE ROYAL INSTITUTION OF GREAT BRITAIN
ON FRIDAY, MAY 31, 1889

NATURE, inert to the eyes of the ancients, has been revealed to us as full of life and activity. The conviction that motion pervaded all things, which was first realised with respect to the stellar universe, has now extended to the unseen world of atoms. No sooner had the human understanding denied to the earth a fixed position and launched it along its path in space, than it was sought to fix immovably the sun and the stars. But astronomy has demonstrated that the sun moves with unswerving regularity through the star-set universe at the rate of about 50 kilometres per second. Among the so-called fixed stars are now discerned manifold changes and various orders of movement. Light, heat, electricity—like sound—have been proved to be modes of motion; to the realisation of this fact modern science is indebted for powers which have been used with such brilliant success, and which have been expounded so clearly at this lecture table by Faraday and by his successors. As, in the imagination of Dante, the invisible air became peopled with spiritual beings, so before the eyes of earnest investigators, and especially before those of Clerk Maxwell, the invisible mass of gases became peopled with particles: their rapid movements, their collisions, and impacts became so manifest that it seemed almost possible to count the impacts and determine many of the peculiarities or laws of their collisions. The fact of the existence of these invisible motions may at once be made apparent by demonstrating the difference in the rate of diffusion through porous bodies of the light and rapidly moving atoms of hydrogen and the heavier and more sluggish particles of air. Within the masses of liquid and of solid bodies we have been forced to acknowledge the existence of persistent though limited motion of their ultimate particles, for otherwise it would be impossible to explain, for example, the celebrated experiments of Graham on diffusion through liquid molecular motion in solid bodies, could the famous Spring have hoped to attain any result by mixing carefully-dried powders of potash, saltpetre and sodium acetate, in order to produce, by pressure, a chemical reaction between these substances through the interchange of their metals, and have derived, for the conviction of the incredulous, a mixture of two hygroscopic though solid salts—sodium nitrate and potassium acetate?

In these invisible and apparently chaotic movements, reaching from the stars to the minutest atoms, there reigns, however, a harmonious order which is commonly mistaken for complete rest, but which is really a consequence of the conservation of that dynamic equilibrium which was first discerned by the genius of Newton, and which has been traced by his successors in the detailed analysis of the particular consequences of the great generalisation, namely, relative immovability in the midst of universal and active movement.

But the unseen world of chemical changes is closely analogous to the visible world of the heavenly bodies, since our atoms form distinct portions of an invisible world, as planets, satellites, and comets form distinct portions of the astronomer's universe; our atoms may therefore be compared to the solar systems, or to the systems of double or of single stars: for example, ammonia (NH_3) may be represented in the simplest manner by supposing the sun, nitrogen, surrounded by its planets of hydrogen; and common salt ($NaCl$) may be looked on as a double star formed of sodium and chlorine. Besides, now that the indestructibility of the elements has been acknowledged, chemical changes cannot otherwise be explained than as changes of motion, and the production by chemical reactions of galvanic currents, of light, of heat, of pressure, or of steam power, demonstrates visibly that the processes of chemical reaction are inevitably connected with enormous though unseen displacements, originating in the movements of atoms in molecules. Astronomers and natural philosophers, in studying the visible motions of the heavenly bodies and of matter on the earth, have understood and have estimated the value of this store of energy. But the chemist has had to pursue a contrary course. Observing in the physical and mechanical phenomena which accompany chemical reactions the quantity of energy manifested by the atoms and molecules, he is constrained to acknowledge that within the molecules there exist atoms in motion, endowed with an energy which, like matter itself, is neither being created nor capable of being destroyed. Therefore, in chemistry, we must seek dynamic equilibrium not only between the molecules, but also in their midst among their component atoms. Many conditions of such equilibrium have been determined, but much remains to be done, and it is not uncommon, even in these days, to find that some chemists forget that there is the possibility of motion in the interior of molecules, and therefore represent them as being in a condition of death-like inactivity.

Chemical combinations take place with so much ease and rapidity, possess so many special characteristics, and are so numerous, that their simplicity and order were for a long time hidden from investigators. Sympathy, relationship, all the caprices or all the fancifulness of human intercourse, seemed to have found complete analogies in chemical combinations, but with this difference, that the characteristics of the material substances—such as silver, for example, or of any other body—remain unchanged in every sub-division from the largest masses to the smallest particles, and consequently these characteristics must be properties of the particles. But the world of heavenly luminaries appeared equally fanciful at man's first acquaintance with it, so much so, that the astrologers imagined a connection between the individualities of men and the conjunctions of planets. Thanks to the genius of Lavoisier and of Dalton, man has been able, in the unseen world of chemical combinations, to recognise laws of the same simple order as those which Copernicus and Kepler proved to exist in the planetary universe. Man discovered, and continues every hour to discover, *what* remains unchanged in chemical evolution, and *how* changes take place in combinations of the unchangeable. He has learned to predict, not only what possible combinations may take place, but also the very existence of atoms of unknown elementary substances, and has besides succeeded in making innumerable practical applications of his knowledge to the great advantage of his race, and has accomplished this notwithstanding that notions of sympathy and affinity still preserve a strong vitality in science. At present we cannot apply Newton's principles to chemistry, because the soil is only being now prepared. The invisible world of chemical atoms is still waiting for the creator of chemical mechanics. For him our age is collecting a mass of materials, the inductions of well-digested facts, and many-sided inferences similar to those which existed for Astronomy and Mechanics in the days of Newton. It is well also to remember that Newton devoted much time to chemical experiments, and while considering questions of celestial mechanics, persistently kept in view the mutual action of those infinitely small worlds which are concerned in chemical evolutions. For this reason, and also to maintain the unity of laws, it seems to me that we must, in the first instance, seek to harmonise the various phases of contemporary chemical theories with the immortal principles of the Newtonian natural philosophy, and so hasten the advent of true chemical mechanics. Let the above considerations serve as my justification for the attempt which I propose to make to act as a champion of the universality of the Newtonian principles, which I believe are competent to embrace every phenomenon in the universe, from the rotation of the fixed stars to the interchanges of chemical atoms.

In the first place I consider it indispensable to bear in mind that, up to quite recent times, only a one-sided affinity has been recognised in chemical reactions. Thus, for example, from the circumstance that red-hot iron decomposes water with the evolution of hydrogen, it was concluded that oxygen had a greater affinity for iron than for hydrogen. But hydrogen, in presence of red-hot iron scale, appropriates its oxygen and forms water, whence an exactly opposite conclusion may be formed.

During the last ten years a gradual, scarcely perceptible, but most important change has taken place in the views, and consequently in the researches, of chemists. They have sought everywhere, and have always found, systems of conservation or dynamic equilibrium substantially similar to those which natural philosophers have long since discovered in the visible world, and in virtue of which the position of the heavenly bodies in the universe is determined. There where one-sided affinities only were at first detected, not only secondary or lateral ones have been found, but even those which are diametrically opposite; yet among these, dynamical equilibrium establishes itself not by excluding one or other of the forces, but regulating them all. So the chemist finds in the flame of the blast furnace, in the formation of every salt, and, with especial clearness, in double salts and in the crystallisation of solutions, not a fight ending in the victory of one side, as used to be supposed, but the conjunction of forces; the peace of dynamic equilibrium resulting from the action of many forces and affinities. Carbonaceous matters, for example, burn at the expense of the oxygen of the air, yielding a quantity of heat, and forming products of combustion, in which it was thought that the affinities of the oxygen with the combustible elements were satisfied. But it appeared that the heat of combustion was competent to decompose these products, to dissociate the oxygen from the combustible elements, and therefore to explain combustion fully it is necessary to take into account the equilibrium between opposite reactions, between those which evolve and those which absorb heat.

In the same way, in the case of the solution of common salt in water, it is necessary to take into account, on the one hand, the formation of compound particles generated by the combination of salt with water, and, on the other, the disintegration or scattering of the new particles formed, as well as of those originally contained. At present we find two currents of thought, apparently antagonistic to each other, dominating the study of solutions: according to the one, solution seems a mere act of building up or association; according to the other, it is only dissociation or disintegration. The truth lies, evidently, between these views; it lies, as I have endeavoured to prove by my investigations into aqueous solutions, in the dynamic equilibrium of particles tending to combine and also to fall asunder. The large majority of chemical reactions which appeared to act victoriously along one line have been proved capable of acting as victoriously even along an exactly opposite line. Elements which utterly decline to combine directly may often be formed into comparatively stable compounds by indirect means, as, for example, in the case of chlorine and carbon; and consequently the sympathies and antipathies which it was thought to transfer from human relations to those of atoms should be laid aside until the mechanism of chemical relations is explained. Let us remember, however, that chlorine, which does not form with carbon the chloride of carbon, is strongly absorbed, or, as it were, dissolved, by carbon, which leads us to suspect incipient chemical action even in an external and purely surface contact, and involuntarily gives rise to conceptions of that unity of the forces of nature which has been so energetically insisted on by Sir William Grove and formulated in his famous paradox. Grove noticed that platinum, when fused in the oxyhydrogen flame, during which operation water is formed, when allowed to drop into water decomposes the latter and produces the explosive oxyhydrogen mixture. The explanation of this paradox, as of many others which arose during the period of chemical renaissance, has led, in our time, to the promulgation by Henri Sainte-Claire Deville of the conception of dissociation and of equilibrium, and has recalled the teaching of Berthollet, which, notwithstanding its brilliant confirmation by Heinrich Rose and Dr. Gladstone, had not, up to that period, been included in received chemical views.

Chemical equilibrium in general, and dissociation in particular, are now being so fully worked out in detail, and supplied in such various ways, that I do not allude to them to develop, but only use them as examples by which to indicate the correctness of a tendency to regard chemical combinations from points of view differing from those expressed by the term hitherto appropriated to define chemical forces, namely, 'affinity.' Chemical equilibria, dissociation, the speed of chemical reactions, thermochemistry, spectroscopy, and, more than all, the determination of the influence of masses and the search for a connection between the properties and weights of atoms and molecules—in one word, the vast mass of the most important chemical researches of the present day--clearly indicate the near approach of the time when chemical doctrines will submit fully and completely to the doctrine which was first announced in the *Principia* of Newton.

In order that the application of these principles may bear fruit it is evidently insufficient to assume that statical equilibrium reigns alone in chemical systems or chemical molecules: it is necessary to grasp the conditions of possible states of dynamical equilibria, and to apply to them kinetic principles. Numerous considerations compel us to renounce the idea of statical equilibrium in molecules, and the recent yet strongly-supported appeals to dynamic principles constitute, in my opinion, the foundation of the modern teaching relating to atomicity, or the valency of the elements, which usually forms the basis of investigations into organic or carbon compounds.

This teaching has led to brilliant explanations of very many chemical relations and to cases of isomerism, or the difference in the properties of substances having the same composition. It has been so fruitful in its many applications and in the foreshadowing of remote consequences, especially respecting carbon compounds, that it is impossible to deny its claims to be ranked as a great achievement of chemical science. Its practical application to the synthesis of many substances of the most complicated composition entering into the structure of organised bodies, and to the creation of an unlimited number of carbon compounds, among which the colours derived from coal tar stand prominently forward, surpass the synthetical powers of Nature itself. Yet this teaching, as applied to the structure of carbon compounds, is not on the face of it directly applicable to the investigation of other elements, because in examining the first it is possible to assume that the atoms of carbon have always a definite and equal number of affinities, whilst in the combinations of other elements this is evidently inadmissible. Thus, for example, an atom of carbon yields only one compound with four atoms of hydrogen and one with four atoms of chlorine in the molecule, whilst the atoms of chlorine and hydrogen unite only in the proportions of one to one. Simplicity is here evident, and forms a point of departure from which it is easy to move forward with firm and secure tread. Other elements are of a different nature. Phosphorus unites with three and with five atoms of chlorine, and consequently the simplicity and sharpness of the application of structural conceptions are lost. Sulphur unites only with two atoms of hydrogen, but with oxygen it enters into higher orders of combination. The periodic relationship which exists among all the properties of the elements—such, for example, as their ability to enter into various combinations—and their atomic weights, indicate that this variation in atomicity is subject to one perfectly exact and general law, and it is only carbon and its near analogues which constitute cases of permanently preserved atomicity. It is impossible to recognise as constant and fundamental properties of atoms, powers which, in substance, have proved to be variable. But by abandoning the idea of permanence, and of the constant saturation of affinities—that is to say, by acknowledging the possibility of free affinities—many retain a comprehension of the atomicity of the elements 'under given conditions;' and on this frail foundation they build up structures composed of chemical molecules, evidently only because the conception of manifold affinities gives, at once, a simple statical method of estimating the composition of the most complicated molecules.

I shall enter neither into details, nor into the various consequences following from these views, nor into the disputes which have sprung up respecting them (and relating especially to the number of isomerides possible on the assumption of free affinities), because the foundation or origin of theories of this nature suffers from the radical defect of being in opposition to dynamics. The molecule, as even Laurent expressed himself, is represented as an architectural structure, the style of which is determined by the fundamental arrangement of a few atoms, whilst the decorative details, which are capable of being varied by the same forces, are formed by the elements entering into the combination. It is on this account that the term 'structural' is so appropriate to the contemporary views of the above order, and that the 'structuralists' seek to justify the tetrahedric, plane, or prismatic disposition of the atoms of carbon in benzene. It is evident that the consideration relates to the statical position of atoms and molecules and not to their kinetic relations. The atoms of the structural type are like the lifeless pieces on a chess board: they are endowed but with the voices of living beings, and are not those living beings themselves; acting, indeed, according to laws, yet each possessed of a store of energy which, in the present state of our knowledge, must be taken into account.

In the days of Haüy, crystals were considered in the same statical and structural light, but modern crystallographers, having become more thoroughly acquainted with their physical properties and their actual formation, have abandoned the earlier views, and have made their doctrines dependent on dynamics.

The immediate object of this lecture is to show that, starting with Newton's third law of motion, it is possible to preserve to chemistry all the advantages arising from structural teaching, without being obliged to build up molecules in solid and motionless figures, or to ascribe to atoms definite limited valencies, directions of cohesion, or affinities. The wide extent of the subject obliges me to treat only a small portion of it, namely of *substitutions*, without specially considering combinations and decompositions, and even then limiting myself to the simplest examples, which, however, will throw open prospects embracing all the natural complexity of chemical relations. For this reason, if it should prove possible to form groups similar, for example, to H_3 or CH_3 as the remnants of molecules CH_4 or C_2H_6 we shall two parts, $H_2 + H_2$ or $CH_4 + H_2$, as soon as they are even temporarily formed, and are incapable of separate existence, and therefore can take no part in the elementary act of substitution. With respect to the simplest molecules which we shall select—that is to say, those of which the parts have no separate existence, and therefore cannot appear in substitutions—we shall consider them according to the periodic law, arranging them in direct dependence on the atomic weight of the elements.

Thus, for example, the molecules of the simplest hydrogen compounds—

HF	H_2O	H_3N	H_4C
hydrofluoric acid	water	ammonia	methane

correspond with elements the atomic weights of which decrease consecutively

$$F = 19, \quad O = 16, \quad N = 14, \quad C = 12.$$

Neither the arithmetical order (1, 2, 3, 4 atoms of hydrogen) nor the total information we possess respecting the elements will permit us to interpolate into this typical series one more additional element; and therefore we have here, for hydrogen compounds, a natural base on which are built up those simple chemical combinations which we take as typical. But even they are competent to unite with each other, as we see, for instance, in the property which hydrofluoric acid has of forming a hydrate—that is, of combining with water; and a similar attribute of ammonia, resulting in the formation of a caustic alkali, NH_3,H_2O, or NH_4OH.

Having made these indispensable preliminary observations, I may now attack the problem itself and attempt to explain the so-called structure or rather construction, of molecules—that is to say, their constitution and transformations—without having recourse to the teaching of 'structuralists,' but on Newton's dynamical principles.

Of Newton's three laws of motion, only the third can be applied directly to chemical molecules when regarded as systems of atoms among which it must be supposed that there exist common influences or forces, and resulting compounded relative motions. Chemical reactions of every kind are undoubtedly accomplished by changes in these internal movements, respecting the nature of which nothing is known at present, but the existence of which the mass of evidence collected in modern times forces us to acknowledge as forming part of the common motion of the universe, and as a fact further established by the circumstance that chemical reactions are always characterised by changes of volume or the relations between the atoms or the molecules. Newton's third law, which is applicable to every system, declares that, 'action is also associated with reaction, and is equal to it.' The brevity of conciseness of this axiom was, however, qualified by Newton in a more expanded statement, 'the action of bodies one upon another are always equal, and in opposite directions.' This simple fact constitutes the point of departure for explaining dynamic equilibrium—that is to say, systems of conservancy. It is capable of satisfying even the dualists, and of explaining, without additional assumptions, the preservation of those chemical types which Dumas, Laurent, and Gerhardt created unit types, and those views of atomic combinations which the structuralists express by atomicity or the valency of the elements, and, in connection with them, the various numbers of affinities. In reality, if a system of atoms or a molecule be given, then in it, according to the third law of Newton, each portion of atoms acts on the remaining portion in the same manner, and with the same force as the second set of atoms acts on the first. We infer directly from this consideration that both sets of atoms, forming a molecule, are not only equivalent with regard to themselves, as they must be according to Dalton's law, but also that they may, if united, replace each other. Let there be a molecule containing atoms A B C, it is clear that, according to Newton's law, the action of A on B C must be equal to the action of B C on A, and if the first action is directed on B C, then the second must be directed on A, and consequently then, where A can exist in dynamic equilibrium, B C may take its place and act in a like manner. In the same way the action of C is equal to the action of A B. In one word every two sets of atoms forming a molecule are equivalent to each other, and may take each other's place in other molecules, or, having the power of balancing each other, the atoms or their complements are endowed with the power of replacing each other. Let us call this consequence of an evident axiom 'the principle of substitution,' and let us apply it to those typical forms of hydrogen compounds which we have already discussed, and which, on account of their simplicity and regularity, have served as starting-points of chemical argument long before the appearance of the doctrine of structure.

In the type of hydrofluoric acid, HF, or in systems of double stars, are included a multitude of the simplest molecules. It will be sufficient for our purpose to recall a few: for example, the molecules of chlorine, Cl_2, and of hydrogen, H_2, and hydrochloric acid, HCl, which is familiar to all in aqueous solution as spirits of salt, and which has many points of resemblance with HF, HBr, HI. In these cases division into two parts can only be made in one way, and therefore the principle of substitution renders it probable that exchanges between the chlorine and the hydrogen can take place, if they are competent to unite with each other. There was a time when no chemist would even admit the idea of any such action; it was then thought that the power of combination indicated a polar difference of the molecules in combination, and this thought set aside all idea of the substitution of one component element by another.

Thanks to the observations and experiments of Dumas and Laurent fifty years ago, such fallacies were dispelled, and in this manner the principle of substitution was exhibited. Chlorine and bromine acting on many hydrogen compounds, occupy immediately the place of their hydrogen, and the displaced hydrogen, with another atom of chlorine or bromine, forms hydrochloric acid or bromide of hydrogen. This takes place in all typical hydrogen compounds. Thus chlorine acts on this principle on gaseous hydrogen—reaction, under the influence of light, resulting in the formation of hydrochloric acid. Chlorine acting on the alkalis, constituted similarly to water, and even on water itself—only, however, under the influence of light and only partially because of the instability of $HClO$—forms by this principle bleaching salts, which are the same as the alkalis, but with their hydrogen replaced by chlorine. In ammonia and in methane chlorine can also replace the hydrogen. From ammonia is formed in this manner the so chloride of nitrogen, NCl_3, which decomposes very readily with violent sion on account of the evolved gases, and falls asunder as chlori nitrogen. Out of marsh gas, or methane, CH_4, may be obtained co tively, by this method, every possible substitution, of which chlor $CHCl_3$, is the best known, and carbon tetrachloride, CCl_4, the most i tive. But by virtue of the fact that chlorine and bromine act, in the r shown, on the simplest typical hydrogen compounds, their action more complicated ones may be assumed to be the same. This can be demonstrated. The hydrogen of benzene, C_6H_6, reacts feebly under th ence of light on liquid bromine, but Gustavson has shown that the a of the smallest quantity of metallic aluminium causes energetic acti the evolution of large volumes of hydrogen bromide.

If we pass on to the second typical hydrogen compound—that is water—its molecule, HOH, may be split up in two ways: either into a of hydrogen and a semi-molecule of hydrogen peroxide, HO, or into o O, and two atoms of hydrogen, H; and therefore, according to the pr of substitution, it is evident that one atom of hydrogen can ex with hydrogen oxide, HO, and two atoms of hydrogen, H, with one a oxygen, O.

Both these forms of substitution will constitute methods of oxid that is to say, of the entrance of oxygen into the compound—a r which is so common in nature as well as in the arts, taking place expense of the oxygen of the air or by the aid of various oxidisin stances or bodies which part easily with their oxygen. There is no o to reckon up the unlimited number of cases of such oxidising reactio is sufficient to state that in the first of these oxygen is directly tran and the position, the chemical function, which hydrogen originally oc is, after the substitution, occupied by the hydroxyl. Thus ammonia yields hydroxylamine, $NH_2(OH)$, a substance which retains many properties of ammonia.

Methane and a number of other hydrocarbons yield, by substitu the hydrogen by its oxide, methyl alcohol, $CH_3(OH)$, and other alcohols substitution of one atom of oxygen for two atoms of hydrogen is common with hydrogen compounds. By this means alcoholic liqui taining ethyl alcohol, or spirits of wine, $C_2H_5(OH)$, are oxidised unt become vinegar, or acetic acid, $C_2H_3O(OH)$. In the same way ammonia, or the combination of ammonia with water, NH_3,H_2O, or N which contains a great deal of hydrogen, by oxidation exchanges four of hydrogen for two atoms of oxygen, and becomes converted into nitr $NO_2(OH)$. This process of conversion of ammonium salts into saltpe on in the fields every summer, and with especial rapidity in tropical co The method by which this is accomplished, though complex, though in the agency of all-permeating micro-organisms, is, in substance, the s that by which alcohol is converted into acetic acid, or glycol, C_2H_4(O oxalic acid, if we view the process of oxidation in the light of the No principles.

But while speaking of the application of the principle of substitu water, we need not multiply instances, but must turn our attention to two special circumstances which are closely connected with the very mechanism of substitutions.

In the first place, the replacement of two atoms of hydrogen by one atom of oxygen may take place in two ways, because the hydrogen molecule is composed of two atoms, and therefore, under the influence of oxygen, the molecule forming water may separate before the oxygen has time to take its place. It is for this reason that we find, during the conversion of alcohol into acetic acid, that there is an interval during which is formed aldehyde, C_2H_4O, which, as its very name implies, is 'alcohol dehydrogenatum,' or alcohol deprived of hydrogen. Hence aldehyde combined with hydrogen yields alcohol; and united to oxygen, acetic acid.

For the same reason there should be, and there actually are, intermediate products between ammonia and nitric acid, $NO_2(HO)$, containing either less hydrogen than ammonia, less oxygen than nitric acid, or less water than caustic ammonia. Accordingly we find, among the products of the deoxidation of nitric acid and the oxidation of ammonia, not only hydroxylamine, but also nitrous oxide, nitrous and nitric anhydrides. Thus, the production of nitrous acid results from the removal of two atoms of hydrogen from caustic ammonia and the substitution of the oxygen for the hydrogen, $NO(OH)$; or by the substitution, in ammonia, of three atoms of hydrogen by hydroxyl, $N(OH)_3$, and by the removal of water: $N(OH)_3 - H_2O = NO(OH)$. The peculiarities and properties of nitrous acid—as, for instance, its action on ammonia and its conversion, by oxidation, into nitric acid—are thus clearly revealed.

On the other hand, in speaking of the principle of substitution as applied to water, it is necessary to observe that hydrogen and hydroxyl, H and OH, are not only competent to unite, but also to form combinations with themselves, and thus become H_2 and H_2O_2; and such are hydrogen and the peroxide thereof. In general, if a molecule A B exists, then molecules A A and B B can exist also. A direct reaction of this kind does not, however, take place in water, therefore undoubtedly, at the moment of formation, hydrogen reacts on hydrogen peroxide, as we can show at once by experiment; and further because hydrogen peroxide, H_2O_2, exhibits a structure containing a molecule of hydrogen, H_2, and one of oxygen, O_2, either of which is capable of separate existence. The fact, however, may now be taken as thoroughly established, that, at the moment of combustion of hydrogen or of the hydrogen compounds, hydrogen peroxide is always formed, and not only so, but in all probability its formation invariably precedes the formation of water. This was to be expected as a consequence of the law of Avogadro and Gerhardt, which leads us to expect this sequence in the case of equal interactions of volumes of vapours and gases; and in hydrogen peroxide we actually have such equal volumes of the elementary gases.

The instability of hydrogen peroxide—that is to say, the ease with which it decomposes into water and oxygen, even at the mere contact of porous substances—accounts for the circumstance that it does not form a permanent product of combustion, and is not produced during the decomposition

of water. I may mention this additional consideration that, with re
to hydrogen peroxide, we may look for its effecting still further sub
tions of hydrogen by means of which we may expect to obtain still
highly oxidised water compounds, such as H_2O_3 and H_2O_4. These Schö
and Bunsen have long been seeking, and Berthelot is investigating
at present. It is probable, however, that the reaction will stop a
last compound, because we find that, in a number of cases, the additi
four atoms of oxygen seems to form a limit. Thus, OsO_4, $KClO_4$, KI
K_2SO_4, Na_3PO_4, and such like, represent the highest grades of oxidation

As for the last forty years, from the times of Berzelius, Dumas, L
Gerhardt, Williamson, Frankland, Kolbe, Kekulé, and Butleroff, most
retical generalisations have centred round organic or carbon compo
we will, for the sake of brevity, leave out the discussion of ammonia d
tives, notwithstanding their simplicity with respect to the doctrine of s
tutions; we will dwell more especially on its application to carbon compo
starting from methane, CH_4, as the simplest of the hydrocarbons, conta
in its molecule one atom of carbon. According to the principles enume
we may derive from CH_4 every combination of the form CH_3X, C
CHX_3, and CX_4, in which X is an element, or radicle, equivalent to hydro
that is to say, competent to take its place or to combine with it. Suc
the chlorine substitutes already mentioned, such is wood-spirit, CH_3(O
which X is represented by the residue of water, and such are numerous
carbon derivatives. If we continue, with the aid of hydroxyl, further s
tutions of the hydrogen of methane we shall obtain successively CH_2(
$CH(OH)_3$, and $C(OH)_4$. But if, in proceeding thus, we bear in min
$CH_2(OH)_2$ contains two hydroxyls in the same form as hydrogen pe
H_2O_2 or $(OH)_2$, contains them—and moreover not only in one molecu
together, attached to one and the same atom of carbon—so here we
look for the same decomposition as that which we find in hydrogen pe
and accompanied also by the formation of water as an indepen
existing molecule; therefore $CH_2(OH)_2$ should yield, as it actually do
mediately water and the oxide of methylene, CH_2O, which is methan

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[1] Because more than four atoms of hydrogen never unite with one atom of
ments, and because the hydrogen compounds (*e.g.* HCl, H_2S, H_3P, H_4Si) alwa
their highest oxides with four atoms of oxygen, and as the highest forms of oxide
RuO_4) also contain four of oxygen, and eight groups of the periodic system, corres
to the highest basic oxides R_2O, RO, R_2O_3, RO_2, R_2O_5, RO_3, R_2O_7, and RO_4, im
above relationship, and because of the nearest analogues among the elements—
Mg, Zn, Cd, and Hg; or Cr, Mo, W, and U; or Si, Ge, Sn, and Pt; or F, Cl, Br
and so forth—not more than four are known, it seems to me that in these relati
there lies a deep interest and meaning with regard to chemical mechanics. But
to my imagination, the idea of unity of design in Nature, either acting in
celestial systems or among chemical molecules, is very attractive, especially bec
atomic teaching at once acquires its true meaning, I will recall the following
lating to the solar system. There are eight major planets, of which the four inn
are not only separated from the four outer by asteroids, but differ from them i
respects, as, for example, in the smallness of their diameters and their greater
Saturn with his ring has eight satellites, Jupiter and Uranus have each four. I
dent that in the solar systems also we meet with these higher numbers four a
which appear in the combination of chemical molecules.

oxygen substituted for two atoms of hydrogen. Exactly in the same manner out of $CH(OH)_3$ are formed water and formic acid, $CHO(OH)$, and out of $C(OH)_4$ is produced water and carbonic acid, or directly carbonic anhydride, CO_2, which will therefore be nothing else than methane with the double replacement of pairs of hydrogen by oxygen. As nothing leads to the supposition that the four atoms of hydrogen in methane differ one from the other, so it does not matter by what means we obtain any one of the combinations indicated—they will be identical; that is to say, there will be no case of actual isomerism, although there may easily be such cases of isomerism as have been distinguished by the term metamerism.

Formic acid, for example, has two atoms of hydrogen, one attached to the carbon left from the methane, and the other attached to the oxygen which has entered in the form of hydroxyl, and if one of them be replaced by some substance X it is evident that we shall obtain substances of the same composition, but of different construction, or of different orders of movement among the molecules, and therefore endowed with other properties and reactions. If X be methyl, CH_3—that is to say, a group capable of replacing hydrogen because it is actually contained with hydrogen in methane itself—then by substituting this group for the original hydrogen we obtain acetic acid, $CCH_3O(OH)$, out of formic, and by substitution of the hydrogen in its oxide or hydroxyl we obtain methyl formate, $CHO(OCH_3)$. These substances differ so much from each other physically and chemically that at first sight it is hardly possible to admit that they contain the same atoms in identically the same proportions. Acetic acid, for example, boils at a higher temperature than water, and has a higher specific gravity than it, whilst its metameride, methyl formate, is lighter than water, and boils at 30°—that is to say, it evaporates very easily.

Let us now turn to carbon compounds containing two atoms of carbon to the molecule, as in acetic acid, and proceed to evolve them from methane by the principle of substitution. This principle declares at once that methane can only be split up in the four following ways:—

1. Into a group CH_3 equivalent with H. Let us call changes of this nature methylation.

2. Into a group CH_2 and H_2. We will call this order of substitutions methylenation.

3. Into CH and H_3, which commutations we will call acetylenation.

4. Into C and H_4, which may be called carbonation.

It is evident that hydrocarbon compounds containing two atoms of carbon can only proceed from methane, CH_4, which contains four atoms of hydrogen by the first three methods of substitution; carbonation would yield free carbon if it could take place directly, and if the molecule of free carbon—which is in reality very complex, that is to say strongly polyatomic, as I have long since been proving by various means—could contain only C_2 like the molecules O_2, H_2, N_2, and so on.

By methylation we should evidently obtain from marsh gas, ethane, $CH_3CH_3 = C_2H_6$.

By methylenation—that is, by substituting group CH_2 for H_2—methane forms ethylene, $CH_2CH_2 = C_2H_4$.

By acetylenation—that is, by substituting three atoms of hydrogen, H_3, in methane—by the remnant CH, we get acetylene, $CHCH = C_2H_2$.

If we have applied the principles of Newton correctly, there should not be any other hydrocarbons containing two atoms of carbon in the molecule. All these combinations have long been known, and in each of them we can not only produce those substitutions of which an example has been given in the case of methane, but also all the phases of other substitutions, as we shall find from a few more instances, by the aid of which I trust that I shall be able to show the great complexity of those derivatives which, on the principle of substitution, can be obtained from each hydrocarbon. Let us content ourselves with the case of ethane, CH_3CH_3, and the substitution of the hydrogen by hydroxyl. The following are the possible changes:—

1. $CH_3CH_2(OH)$: this is nothing more than spirit of wine, or ethyl alcohol, $C_2H_5(OH)$ or C_2H_6O.

2. $CH_2(OH)CH_2(OH)$: this is the glycol of Würtz, which has shed so much light on the history of alcohol. Its isomeride may be $CH_3CH(OH)_2$, but as we have seen in the case of $CH(OH)_2$, it decomposes, giving off water, and forming aldehyde, CH_3CHO, a substance capable of yielding alcohol by uniting with hydrogen, and of yielding acetic acid by uniting with oxygen.

If glycol, $CH_2(OH)CH_2(OH)$, loses its water, it may be seen at once that it will not now yield aldehyde, CH_3CHO, but its isomeride, $\underset{O}{CH_2CH_2}$, the oxide of ethylene. I have here indicated in a special manner the oxygen which has taken the place of two atoms of the hydrogen of ethane taken from different atoms of the carbon.

3. $CH_3C(OH)_3$ decomposed as $CH(OH)_3$, forming water and acetic acid, $CH_3CO(OH)$. It is evident that this acid is nothing else than formic acid, $CHO(OH)$, with its hydrogen replaced by methyl. Without examining further the vast number of possible derivatives, I will direct your attention to the circumstance that in dissolving acetic acid in water we obtain the maximum contraction and the greatest viscosity when to the molecule $CH_3CO(OH)$ is added a molecule of water, which is the proportion which would form the hydrate $CH_3C(OH)_3$. It is probable that the doubling of the molecule of acetic acid at temperatures approaching its boiling-point has some connection with this power of uniting with one molecule of water.

4. $CH_2(OH)C(OH)_3$ is evidently an alcoholic acid, and indeed this compound, after losing water, answers to glycolic acid, $CH_2(OH)CO(OH)$. Without investigating all the possible isomerides, we will note only that the hydrate $CH(OH)_2CH(OH)_2$ has the same composition as $CH_2(OH)C(OH)_3$, and although corresponding to glycol, and being a symmetrical substance, it becomes, on parting with its water, the aldehyde of oxalic acid, or the glyoxal of Debus, $CHOCHO$.

5. $CH(OH)_2C(OH_3)$, from the tendency of all the preceding, corresponds with glyoxylic acid, an aldehyde acid, $CHOCO(OH)$, because the group $CO(OH)$, or carboxyl, enters into the compositions of organic acids, and the group CHO defines the aldehyde function.

6. $C(OH)_3C(OH)_3$ through the loss of $2H_2O$ yields the bibasic oxalic acid

$CO(OH)CO(OH)$, which generally crystallises with $2H_2O$, following thus the normal type of hydration characteristic of ethane.[2]

Thus, by applying the principle of substitution, we can, in the simplest manner, derive not only every kind of hydrocarbon compound, such as the alcohols, the aldehyde-alcohols, aldehydes, alcohol-acids, and the acids, but also combinations analogous to hydrated crystals which usually are disregarded.

But even those unsaturated substances, of which ethylene, CH_2CH_2, and acetylene, $CHCH$, are types, may be evolved with equal simplicity. With respect to the phenomena of isomerism, there are many possibilities among the hydrocarbon compounds containing two atoms of carbon, and without going into details it will be sufficient to indicate that the following formulæ, though not identical, will be isomeric substantially among themselves:—CH_3CHX_2 and CH_2XCH_2X, although both contain $C_2H_4X_2$; or CH_2CX_2 and $CHXCHX$, although both contain $C_2H_2X_2$, if by X we indicate chlorine or generally an element capable of replacing one atom of hydrogen, or capable of uniting with it. To isomerism of this kind belongs the case of aldehyde and the oxide of ethylene, to which we have already referred, because both have the composition C_2H_4O.

What I have said appears to me sufficient to show that the principle of substitution adequately explains the composition, the isomerism, and all the diversity of combination of the hydrocarbons, and I shall limit the further development of these views to preparing a complete list of every possible hydrocarbon compound containing three atoms of carbon in the molecule. There are eight in all, of which only five are known at present.[3]

Among those possible for C_3H_6 there should be two isomerides, propylene and trimethylene, and they are both already known. For C_3H_4 there should be three isomerides: allylene and allene are known, but the third has not yet been discovered; and for C_3H_2 there should be two isomerides, though neither of them is known as yet. Their composition and structure are easily deduced from ethane, ethylene, and acetylene, by methylation, by methylenation, by acetylenation and by carbonation.

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[2] One more isomeride, $CH_3CH(OH)$, is possible—that is, secondary vinyl alcohol, which is related to ethylene, CH_2CH_2, but derived by the principle of substitution from CH_4. Other isomerides, of the composition C_2H_4O, such, for example, as $CCH_3(OH)$, are impossible, because it would correspond with the hydrocarbon $CHCH_3 = C_2H_4$, which is isomeric with ethylene, and it cannot be derived from methane. If such an isomeride existed it would be derived from CH_2, but such products are, up to the present, unknown. In such cases the insufficiency of the points of departure of the statical structural teaching is shown. It first admits constant atomicity and then rejects it, the facts serving to establish either one or the other view; and therefore it seems to me that we must come to the conclusion that the structural method of reasoning, having done a service to science, has outlived the age, and must be regenerated, as in their time was the teaching of the electro-chemists, the radicalists, and the adherents of the doctrine of types. As we cannot now lean on the views above stated, it is time to abandon the structural theory They will all be united in chemical mechanics, and the principle of substitution must be looked on only as a preparation for the coming epoch in chemistry, where such cases as the isomerism of fumaric and maleic acids, when explained dynamically, as proposed by Le Bel and Van't Hoff, may yield points of departure.

[3] Conceding variable atomicity, the structuralists must expect an incomparably larger number of isomerides, and they cannot now decline to acknowledge the change of atomicity, were it only for the examples $HgCl$ and $HgCl_2$, CO and CO_2, PCl_3 and PCl_5.

1. $C_3H_8 = CH_3CH_2CH_3$ out of CH_3CH_3 by methylation. This hydrocarbon is named propane.

2. $C_3H_6 = CH_3CHCH_2$ out of CH_3CH_3 by methylenation. This substance is propylene.

3. $C_3H_6 = CH_2CH_2CH_2$ out of CH_3CH_3 by methylenation. This substance is trimethylene.

4. $C_3H_4 = CH_3CCH$ out of CH_3CH_3 by acetylenation or from CHCH by methylation. This hydrocarbon is named allylene.

5. $C_3H_4 =$ $\begin{matrix}CHCH\\CH_2\end{matrix}$ out of CH_3CH_3 by acetylenation, or from CH_2CH_2 by methylenation, because $\begin{matrix}CH_2CH\\CH\end{matrix} = \begin{matrix}CHCH\\CH_2\end{matrix}$ This body is as yet unknown.

6. $C_3H_4 = CH_2CCH_2$ out of CH_2CH_2 by methylenation. This hydrocarbon is named allene, or iso-allylene.

7. $C_3H_2 =$ $\begin{matrix}CHCH\\C\end{matrix}$ out of CH_3CH_3 by symmetrical carbonation, or out of CH_2CH_2 by acetylenation. This compound is unknown.

8. $C_3H_2 =$ $\begin{matrix}CC\\CH_2\end{matrix}$ out of CH_3CH_3 by carbonation, or out of CHCH by methylenation. This compound is unknown.

If we bear in mind that for each hydrocarbon serving as a type in the above tables there are a number of corresponding derivatives, and that every compound obtained may, by further methylation, methylenation, acetylenation, and carbonation, produce new hydrocarbons, and these may be followed by a numerous suite of derivatives and an immense number of isomeric substances, it is possible to understand the limitless number of carbon compounds, although they all have the one substance, methane, for their origin. The number of substances is so enormous that it is no longer a question of enlarging the possibilities of discovery, but rather of finding some means of testing them analogous to the well-known two which for a long time have served as gauges for all carbon compounds.

I refer to the law of even numbers and to that of limits, the first enunciated by Gerhardt some forty years ago, with respect to hydrocarbons, namely, that their molecules always contain an even number of atoms of hydrogen. But by the method which I have used of deriving all the hydrocarbons from methane, CH_4, this law may be deduced as a direct consequence of the principle of substitutions. Accordingly, in methylation, CH_3 takes the place of H, and therefore CH_2 is added. In methylenation the number of atoms of hydrogen remains unchanged, and at each acetylenation it is reduced by two, and in carbonation by four, atoms—that is to say, an even number of atoms of hydrogen is always added or removed. And because the fundamental hydrocarbon, methane, CH_4, contains an even number of atoms of hydrogen, all its derivative hydrocarbons will also contain even numbers of hydrogen, and this constitutes the law of even numbers.

The principle of substitutions explains with equal simplicity the conception of the limiting compositions of hydrocarbons C_nH_{2n+2}, which I derived, in

1861,[4] in an empirical manner from accumulated materials available at that time, and on the basis of the limits to combinations worked out by Dr. Frankland for other elements.

Of all the various substitutions the highest proportion of hydrogen is yielded by methylation, because in that operation alone does the quantity of hydrogen increase; hence, taking methane as a point of departure, if we imagine methylation effected $(n - 1)$ times, we obtain hydrocarbon compounds containing the highest quantities of hydrogen. It is evident that they will contain $CH_4 + (n - 1)CH_2$, or C_nH_{2n+2}, because methylation leads to the addition of CH_2 to the compound.

It will thus be seen that by the principle of substitution—that is to say, by the third law of Newton—we are able to deduce, in the simplest manner, not only the individual composition, the isomerism, and relations of substances, but also the general laws which govern their most complex combinations without having recourse either to statical constructions, to the definition of atomicities, to the exclusion of free affinities, or to the recognition of those single, double or treble bonds which are so indispensable to structuralists in the explanation of the composition and construction of hydrocarbon compounds. And yet, by the application of the dynamical principles of Newton, we can attain to that chief and fundamental object, the comprehension of isomerism in hydrocarbon compounds, and the forecasting of the existence of combinations as yet unknown, by which the edifice raised by structural teaching is strengthened and supported. Besides—and I count this for a circumstance of special importance—the process which I advocate will make no difference in those special cases which have been already so well worked out, such as, for example, the isomerism of the hydrocarbons and alcohols, even to the extent of not interfering with the nomenclature which has been adopted, and the structural system will retain all the glory of having worked up, in a thoroughly scientific manner, the store of information which Gerhardt had accumulated about the middle of the fifties, and the still higher glory of establishing the rational synthesis of organic substances. Nothing will be lost to the structural doctrine except its statical origin; and as soon as it will embrace the dynamic principles of Newton, and suffer itself to be guided by them, I believe that we shall attain for chemistry that unity of principle, which is now wanting. Many an adept will be attracted to that brilliant and fascinating enterprise, the penetration into the unseen world of the kinetic relations of atoms, to the study of which the last twenty-five years have contributed so much labour and such high inventive faculties.

D'Alembert found in mechanics that if inertia be taken to represent force, dynamic equations may be applied to statical questions, which are thereby rendered more simple and more easily understood.

The structural doctrine in chemistry has unconsciously followed the same course, and therefore its terms are easily adopted; they may retain their present forms provided that a truly dynamical—that is to say, Newtonian—meaning be ascribed to them.

Before finishing my task and demonstrating the possibility of adapting

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Essai d'une théorie sur les limites des combinaisons organiques,' par D. Mendeléeff, 2/11 août 1861, *Bulletin de l'Académie i. d. Sc. de St. Pétersbourg*, t. v

structural doctrines to the dynamics of Newton, I consider it indispensable to touch on one question which naturally arises, and which I have heard discussed more than once. If bromine, the atom of which is eighty times heavier than that of hydrogen, takes the place of hydrogen, it would seem that the whole system of dynamic equilibrium must be destroyed.

Without entering into the minute analysis of this question, I think it will be sufficient to examine it by the light of two well-known phenomena, one of which will be found in the department of chemistry and the other in that of celestial mechanics, and both will serve to demonstrate the existence of that unity in the plan of creation which is a consequence of the Newtonian doctrines. Experiments demonstrate that when a heavy element is substituted for a light one in a chemical compound—for example, for magnesium, in the oxide of that metal, an atom of mercury, which is 8⅓ times heavier—the chief chemical characteristics or properties are generally, though not always, preserved.

The substitution of silver for hydrogen, than which it is 108 times heavier, does not affect all the properties of the substance, though it does some. Therefore chemical substitutions of this kind—the substitution of light for heavy atoms—need not necessarily entail changes in the original equilibrium; and this point is still further elucidated by the consideration that the periodic law indicates the degree of influence of an increment of weight in the atom as affecting the possible equilibria, and also what degree of increase in the weight of the atoms reproduces some, though not all, of the properties of the substance.

This tendency to repetition—these periods—may be likened to those annual or diurnal periods with which we are so familiar on the earth. Days and years follow each other, but, as they do so, many things change; and in like manner chemical evolutions, changes in the masses of the elements, permit of much remaining undisturbed, though many properties undergo alteration. The system is maintained according to the laws of conservation in nature, but the motions are altered in consequence of the change of parts.

Next, let us take an astronomical case—such, for example, as the earth and the moon—and let us imagine that the mass of the latter is constantly increasing. The question is, what will then occur? The path of the moon in space is a wave-line similar to that which geometricians have named epicycloidal, or the locus of a point in a circle rolling round another circle. But in consequence of the influence of the moon it is evident that the path of the earth itself cannot be a geometric ellipse, even supposing the sun to be immovably fixed; it must be an epicycloidal curve, though not very far removed from the true ellipse—that is to say, it will be impressed with but faint undulations. It is only the common centre of gravity of the earth and the moon which describes a true ellipse round the sun. If the moon were to increase, the relative undulations of the earth's path would increase in amplitude, those of the moon would also change, and when the mass of the moon had increased to an equality with that of the earth, the path would consist of epicycloidal curves crossing each other, and having opposite phases. But a similar relation exists between the sun and the earth, because the former is also moving in space. We may apply these views to the world of atoms, and suppose that in their movements, when heavy ones take the place of those that are lighter, similar changes take place, provided that the system or the molecule is preserved throughout the change.

It seems probable that in the heavenly systems, during incalculable astronomical periods, changes have taken place and are still going on similar to those which pass rapidly before our eyes during the chemical reaction of molecules, and the progress of molecular mechanics may—we hope will—in course of time permit us to explain those changes in the stellar world which have more than once been noticed by astronomers, and which are now so carefully studied. A coming Newton will discover the laws of these changes. Those laws, when applied to chemistry, may exhibit peculiarities, but these will certainly be mere variations on the grand harmonious theme which reigns in nature. The discovery of the laws which produce this harmony in chemical evolution will only be possible, it seems to me, under the banner of Newtonian dynamics, which has so long waved over the domains of mechanics, astronomy, and physics. In calling chemists to take their stand under its peaceful and catholic shadow I imagine that I am aiding in establishing that scientific union which the managers of the Royal Institution wish to effect, who have shown their desire to do so by the flattering invitation which has given me—a Russian—the opportunity of laying before the countrymen of Newton an attempt to apply to chemistry one of his immortal principles.

APPENDIX II

THE PERIODIC LAW OF THE CHEMICAL ELEMENTS

By PROFESSOR MENDELÉEFF

FARADAY LECTURE DELIVERED BEFORE THE FELLOWS OF
THE CHEMICAL SOCIETY IN THE THEATRE OF THE ROYAL INSTITUTION,
ON TUESDAY, JUNE 4, 1889

The high honour bestowed by the Chemical Society in inviting me to pay a tribute to the world-famed name of Faraday by delivering this lecture has induced me to take for its subject the Periodic Law of the Elements—this being a generalisation in chemistry which has of late attracted much attention.

While science is pursuing a steady onward movement, it is convenient from time to time to cast a glance back on the route already traversed, and especially to consider the new conceptions which aim at discovering the general meaning of the stock of facts accumulated from day to day in our laboratories. Owing to the possession of laboratories, modern science now bears a new character, quite unknown, not only to antiquity, but even to the preceding century. Bacon's and Descartes' idea of submitting the mechanism of science simultaneously to experiment and reasoning has been fully realised in the case of chemistry, it having become not only possible but always customary to experiment. Under the all-penetrating control of experiment, a new theory, even if crude, is quickly strengthened, provided it be founded on a sufficient basis; the asperities are removed, it is amended by degrees, and soon loses the phantom light of a shadowy form or of one founded on mere prejudice; it is able to lead to logical conclusions, and to submit to experimental proof. Willingly or not, in science we all must submit not to what seems to us attractive from one point of view or from another, but to what represents an agreement between theory and experiment; in other words, to demonstrated generalisation and to the approved experiment. Is it long since many refused to accept the generalisations involved in the law of Avogadro and Ampère, so widely extended by Gerhardt? We still may hear the

The striking observations with the spectroscope which have permitted us to analyse the chemical constitution of distant worlds, seemed, at first, applicable to the task of determining the nature of the atoms themselves; but the working out of the idea in the laboratory soon demonstrated that the characters of spectra are determined, not directly by the atoms, but by the molecules into which the atoms are packed; and so it became evident that more verified facts must be collected before it will be possible to formulate new generalisations capable of taking their place beside those ordinary ones based upon the conception of simple substances and atoms. But as the shade of the leaves and roots of living plants, together with the relics of a decayed vegetation, favour the growth of the seedling and serve to promote its luxurious development, in like manner sound generalisations—together with the relics of those which have proved to be untenable—promote scientific productivity, and ensure the luxurious growth of science under the influence of rays emanating from the centres of scientific energy. Such centres are scientific associations and societies. Before one of the oldest and most powerful of these I am about to take the liberty of passing in review the twenty years' life of a generalisation which is known under the name of the Periodic Law. It was in March 1869 that I ventured to lay before the then youthful Russian Chemical Society the ideas upon the same subject which I had expressed in my just written 'Principles of Chemistry.'

Without entering into details, I will give the conclusions I then arrived at in the very words I used:—

'1. The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

'2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (*e.g.* platinum, iridium, osmium) or which increase regularly (*e.g.* potassium, rubidium, cæsium).

'3. The arrangement of the elements, or of groups of elements, in the order of their atomic weights, corresponds to their so-called *valencies* as well as, to some extent, to their distinctive chemical properties—as is apparent, among other series, in that of lithium, beryllium, barium, carbon, nitrogen, oxygen, and iron.

'4. The elements which are the most widely diffused have *small* atomic weights.

'5. The *magnitude* of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound.

'6. We must expect the discovery of many yet *unknown* elements—for example, elements analogous to aluminium and silicon, whose atomic weight would be between 65 and 75.

'7. The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus, the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.

'8. Certain characteristic properties of the elements can be foretold from their atomic weights.

'The aim of this communication will be fully attained if I succeed in drawing the attention of investigators to those relations which exist between the atomic weights of dissimilar elements, which, so far as I know, have hitherto been almost completely neglected. I believe that the solution of some of the most important problems of our science lies in researches of this kind.'

To-day, twenty years after the above conclusions were formulated, they may still be considered as expressing the essence of the now well-known periodic law.

Reverting to the epoch terminating with the sixties, it is proper to indicate three series of data without the knowledge of which the periodic law could not have been discovered, and which rendered its appearance natural and intelligible.

In the first place, it was at that time that the numerical value of atomic weights became definitely known. Ten years earlier such knowledge did not exist, as may be gathered from the fact that in 1860 chemists from all parts of the world met at Karlsruhe in order to come to some agreement, if not with respect to views relating to atoms, at any rate as regards their definite representation. Many of those present probably remember how vain were the hopes of coming to an understanding, and how much ground was gained at that Congress by the followers of the unitary theory so brilliantly represented by Cannizzaro. I vividly remember the impression produced by his speeches, which admitted of no compromise, and seemed to advocate truth itself, based on the conceptions of Avogadro, Gerhardt, and Regnault, which at that time were far from being generally recognised. And though no understanding could be arrived at, yet the objects of the meeting were attained, for the ideas of Cannizzaro proved, after a few years, to be the only ones which could stand criticism, and which represented an atom as—'the smallest portion of an element which enters into a molecule of its compound.' Only such real atomic weights—not conventional ones—could afford a basis for generalisation. It is sufficient, by way of example, to indicate the following cases in which the relation is seen at once and is perfectly clear:—

K = 39 Rb = 85 Cs = 133
Ca = 40 Sr = 87 Ba = 137

whereas with the equivalents then in use—

K = 39 Rb = 85 Cs = 133
Ca = 20 Sr = 43·5 Ba = 68·5

the consecutiveness of change in atomic weight, which with the true values is so evident, completely disappears.

Secondly, it had become evident during the period 1860–70, and even during the preceding decade, that the relations between the atomic weights of analogous elements were governed by some general and simple laws. Cooke, Cremers, Gladstone, Gmelin, Lenssen, Pettenkofer, and especially Dumas, had already established many facts bearing on that view. Thus Dumas compared the following groups of analogous elements with organic radicles:—

	Diff.		Diff.		Diff.		Diff.
		Mg = 12		P = 31		O = 8	
			8		44		8
Li = 7		Ca = 20		As = 75		S = 16	
	16		3 × 8		44		3 × 8
Na = 23		Sr = 44		Sb = 119		Se = 40	
	16		3 × 8		2 × 44		3 × 8
K = 39		Ba = 68		Bi = 207		Te = 64	

and pointed out some really striking relationships, such as the following:—

F = 19.
Cl = 35·5 = 19 + 16·5
Br = 80 = 19 + 2 × 16·5 + 28.
I = 127 = 2 × 19 + 2 × 16·5 + 2 × 28.

A. Strecker, in his work 'Theorien und Experimente zur Bestimmung der Atomgewichte der Elemente' (Braunschweig, 1859), after summarising the data relating to the subject, and pointing out the remarkable series of equivalents—

Cr = 26·2 Mn = 27·6 Fe = 28 Ni = 29 Co = 30 Cu = 31·7
Zn = 32·5

remarks that: 'It is hardly probable that all the above-mentioned relations between the atomic weights (or equivalents) of chemically analogous elements are merely accidental. We must, however, leave to the future the discovery of the *law* of the relations which appears in these figures.'[1]

In such attempts at arrangement and in such views are to be recognised the real forerunners of the periodic law; the ground was prepared for it between 1860 and 1870, and that it was not expressed in a determinate form before the end of the decade may, I suppose, be ascribed to the fact that only analogous elements had been compared. The idea of seeking for a relation between the atomic weights of all the elements was foreign to the ideas then current, so that neither the *vis tellurique* of De Chancourtois, nor the *law of octaves* of Newlands, could secure anybody's attention. And yet both De Chancourtois and Newlands like Dumas and Strecker, more than Lenssen and Pettenkofer, had made an approach to the periodic law and had discovered its germs. The solution of the problem advanced but slowly, because the facts, but not the law, stood foremost in all attempts; and the law could not awaken a general interest so long as elements, having no apparent connection with each other, were included in the same octave, as for example:—

1st octave of Newlands . .	H	F	Cl	Co & Ni	Br	Pd	I	Pt & Ir
7th Ditto	O	S	Fe	Se	Rh & Ru	Te	Au	Os or Th

Analogies of the above order seemed quite accidental, and the more so as the octave contained occasionally ten elements instead of eight, and when two such elements as Ba and V, Co and Ni, or Rh and Ru, occupied one place in the octave.[3] Nevertheless, the fruit was ripening, and I now see clearly that Strecker, De Chancourtois, and Newlands stood foremost in the way towards the discovery of the periodic law, and that they merely wanted the boldness necessary to place the whole question at such a height that its reflection on the facts could be clearly seen.

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[1] 'Es ist wohl kaum anzunehmen, dass alle im Vorhergehenden hervorgehobenen Beziehungen zwischen den Atomgewichten (oder Aequivalenten) in chemischen Verhältnissen einander ähnliche Elemente bloss zufällig sind. Die Auffindung der in diesen Zahlen *gesetzlichen* Beziehungen müssen wir jedoch der Zukunft überlassen.'

A third circumstance which revealed the periodicity of chemical elements was the accumulation, by the end of the sixties, of new information respecting the rare elements, disclosing their many-sided relations to the other elements and to each other. The researches of Marignac on niobium, and those of Roscoe on vanadium, were of special moment. The striking analogies between vanadium and phosphorus on the one hand, and between vanadium and chromium on the other, which became so apparent in the investigations connected with that element, naturally induced the comparison of $V=51$ with $Cr=52$, $Nb=94$ with $Mo=96$, and $Ta=192$ with $W=194$; while, on the other hand, $P=31$ could be compared with $S=32$, $As=75$ with $Se=79$, and $Sb=120$ with $Te=125$. From such approximations there remained but one step to the discovery of the law of periodicity.

The law of periodicity was thus a direct outcome of the stock of generalisations and established facts which had accumulated by the end of the decade 1860–1870: it is an embodiment of those data in a more or less systematic expression. Where, then, lies the secret of the special importance which has since been attached to the periodic law, and has raised it to the position of a generalisation which has already given to chemistry unexpected aid, and which promises to be far more fruitful in the future and to impress upon several branches of chemical research a peculiar and original stamp? The remaining part of my communication will be an attempt to answer this question.

In the first place we have the circumstance that, as soon as the law made its appearance, it demanded a revision of many facts which were considered by chemists as fully established by existing experience. I shall return, later on, briefly to this subject, but I wish now to remind you that the periodic law, by insisting on the necessity for a revision of supposed facts, exposed itself at once to destruction in its very origin. Its first requirements, however, have been almost entirely satisfied during the last 20 years; the supposed facts have yielded to the law, thus proving that the law itself was a legitimate induction from the verified facts. But our inductions from data have often to do with such details of a science so rich in facts, that only generalisations which cover a wide range of important phenomena can attract general attention. What were the regions touched on by the periodic law? This is what we shall now consider.

The most important point to notice is, that periodic functions, used for the purpose of expressing changes which are dependent on variations of time and space, have been long known. They are familiar to the mind when we have to deal with motion in closed cycles, or with any kind of deviation from a stable position, such as occurs in pendulum-oscillations. A like periodic function became evident in the case of the elements, depending on the mass of the atom. The primary conception of the masses of bodies, or of the masses of atoms, belongs to a category which the present state of science forbids us to discuss, because as yet we have no means of dissecting or analysing the conception. All that was known of functions dependent on masses derived its origin from Galileo and Newton, and indicated that such functions either decrease or increase with the increase of mass, like the attraction of celestial bodies. The numerical expression of the phenomena was always found to be proportional to the mass, and in no case was an increase of mass followed by a recurrence of properties such as is disclosed by the periodic law of the elements. This constituted such a novelty in the study of the phenomena of nature that, although it did not lift the veil which conceals the true conception of mass, it nevertheless indicated that the explanation of that conception must be searched for in the masses of the atoms; the more so, as all masses are nothing but aggregations, or additions, of chemical atoms which would be best described as chemical individuals. Let me remark, by the way, that though the Latin word 'individual' is merely a translation of the Greek word 'atom,' nevertheless history and custom have drawn a sharp distinction between the two words, and the present chemical conception of atoms is nearer to that defined by the Latin word than by the Greek, although this latter also has acquired a special meaning which was unknown to the classics. The periodic law has shown that our chemical individuals display a harmonic periodicity of properties dependent on their masses. Now natural science has long been accustomed to deal with periodicities observed in nature, to seize them with the vice of mathematical analysis, to submit them to the rasp of experiment. And these instruments of scientific thought would surely, long since, have mastered the problem connected with the chemical elements, were it not for a new feature which was brought to light by the periodic law, and which gave a peculiar and original character to the periodic function.

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[3] To judge from J. A. R. Newlands's work, *On the Discovery of the Periodic Law*, London, 1884, p. 149; 'On the Law of Octaves' (from the *Chemical News*, 12, 83, August 18, 1865).

If we mark on an axis of abscissæ a series of lengths proportional to angles, and trace ordinates which are proportional to sines or other trigonometrical functions, we get periodic curves of a harmonic character. So it might seem, at first sight, that with the increase of atomic weights the function of the properties of the elements should also vary in the same harmonious way. But in this case there is no such continuous change as in the curves just referred to, because the periods do not contain the infinite number of points constituting a curve, but a *finite* number only of such points. An example will better illustrate this view. The atomic weights—

Ag = 108 Cd = 112 In = 113 Sn = 118 Sb = 120
Te = 125 I = 127

steadily increase, and their increase is accompanied by a modification of many properties which constitutes the essence of the periodic law. Thus, for example, the densities of the above elements decrease steadily, being respectively—

10·5 8·6 7·4 7·2 6·7 6·4 4·9

while their oxides contain an increasing quantity of oxygen—

$$Ag_2O \qquad Cd_2O_2 \qquad In_2O_3 \qquad Sn_2O_4 \qquad Sb_2O_5 \qquad Te_2O_6 \qquad I_2O_7$$

But to connect by a curve the summits of the ordinates expressing any of these properties would involve the rejection of Dalton's law of multiple proportions. Not only are there no intermediate elements between silver, which gives AgCl, and cadmium, which gives $CdCl_2$, but, according to the very essence of the periodic law, there can be none; in fact a uniform curve would be inapplicable in such a case, as it would lead us to expect elements possessed of special properties at any point of the curve. The periods of the elements have thus a character very different from those which are so simply represented by geometers. They correspond to points, to numbers, to sudden changes of the masses, and not to a continuous evolution. In these sudden changes destitute of intermediate steps or positions, in the absence of elements intermediate between, say, silver and cadmium, or aluminium and silicon, we must recognise a problem to which no direct application of the analysis of the infinitely small can be made. Therefore, neither the trigonometrical functions proposed by Ridberg and Flavitzky, nor the pendulum-oscillations suggested by Crookes, nor the cubical curves of the Rev. Mr. Haughton, which have been proposed for expressing the periodic law, from the nature of the case, can represent the periods of the chemical elements. If geometrical analysis is to be applied to this subject, it will require to be modified in a special manner. It must find the means of representing in a special way, not only such long periods as that comprising

K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br,

but short periods like the following:—

Na Mg Al Si P S Cl.

In the theory of numbers only do we find problems analogous to ours, and two attempts at expressing the atomic weights of the elements by algebraic formulæ seem to be deserving of attention, although neither of them can be considered as a complete theory, nor as promising finally to solve the problem of the periodic law. The attempt of E. J. Mills (1886) does not even aspire to attain this end. He considers that all atomic weights can be expressed by a logarithmic function,

$$15(n - 0{\cdot}9375^t),$$

in which the variables n and t are *whole numbers*. Thus, for oxygen, $n = 2$, and $t = 1$, whence its atomic weight is $= 15{\cdot}94$; in the case of chlorine, bromine, and iodine, n has respective values of 3, 6, and 9, whilst $t = 7, 6,$ and 9; in the case of potassium, rubidium, and cæsium, $n = 4, 6,$ and 9, and $t = 14, 18,$ and 20.

Another attempt was made in 1888 by B. N. Tchitchérin. Its author places the problem of the periodic law in the first rank, but as yet he has investigated the alkali metals only Tchitchérin first noticed the simple relations existing between the atomic volumes of all alkali metals; they can be expressed, according to his views, by the formula

$$A(2-0{\cdot}00535An),$$

where A is the atomic weight, and n is equal to 8 for lithium and sodium, to 4 for potassium, to 3 for rubidium, and to 2 for cæsium. If n remained equal to 8 during the increase of A, the volume would become zero at A = 46⅔, and it would reach its maximum at A = 23⅓. The close approximation of the number 46⅔ to the differences between the atomic weights of analogous elements (such as Cs − Rb, I − Br, and so on); the close correspondence of the number 23⅓ to the atomic weight of sodium; the fact of n being necessarily a whole number, and several other aspects of the question, induce Tchitchérin to believe that they afford a clue to the understanding of the nature of the elements; we must, however, await the full development of his theory before pronouncing judgment on it. What we can at present only be certain of is this: that attempts like the two above named must be repeated and multiplied, because the periodic law has clearly shown that the masses of the atoms increase abruptly, by steps, which are clearly connected in some way with Dalton's law of multiple proportions; and because the periodicity of the elements finds expression in the transition from RX to RX_2, RX_3, RX_4, and so on till RX_8, at which point, the energy of the combining forces being exhausted, the series begins anew from RX to RX_2, and so on.

While connecting by new bonds the theory of the chemical elements with Dalton's theory of multiple proportions, or atomic structure of bodies, the periodic law opened for natural philosophy a new and wide field for speculation. Kant said that there are in the world 'two things which never cease to call for the admiration and reverence of man: the moral law within ourselves, and the stellar sky above us.' But when we turn our thoughts towards the nature of the elements and the periodic law, we must add a third subject, namely, 'the nature of the elementary individuals which we discover everywhere around us.' Without them the stellar sky itself is inconceivable; and in the atoms we see at once their peculiar individualities, the infinite multiplicity of the individuals, and the submission of their seeming freedom to the general harmony of Nature.

Having thus indicated a new mystery of Nature, which does not yet yield to rational conception, the periodic law, together with the revelations of spectrum analysis, have contributed to again revive an old but remarkably long-lived hope—that of discovering, if not by experiment, at least by a mental effort, the *primary matter*—which had its genesis in the minds of the Grecian philosophers, and has been transmitted, together with many other ideas of the classic period, to the heirs of their civilisation. Having grown, during the times of the alchemists up to the period when experimental proof was required, the idea has rendered good service; it induced those careful observations and experiments which later on called into being the works of Scheele, Lavoisier, Priestley, and Cavendish. It then slumbered awhile, but was soon awakened by the attempts either to confirm or to refute the ideas of Prout as to the multiple proportion relationship of the atomic weights of all the elements. And once again the inductive or experimental method of studying Nature gained a direct advantage from the old Pythagorean idea: because atomic weights were determined with an accuracy formerly unknown. But again the idea could not stand the ordeal of experimental test, yet the prejudice remains and has not been uprooted, even by Stas; nay, it has gained a new vigour, for we see that all which is imperfectly worked out, new and unexplained, from the still scarcely studied rare metals to the hardly perceptible nebulæ, have been used to justify it. As soon as spectrum analysis appears as a new and powerful weapon of chemistry, the idea of a primary matter is immediately attached to it. From all sides we see attempts to constitute the imaginary substance *helium*[3] the so much longed for primary matter. No attention is paid to the circumstance that the helium line is only seen in the spectrum of the solar protuberances, so that its universality in Nature remains as problematic as the primary matter itself; nor to the fact that the helium line is wanting amongst the Fraunhofer lines of the solar spectrum, and thus does not answer to the brilliant fundamental conception which gives its real force to spectrum analysis.

And finally, no notice is even taken of the indubitable fact that the brilliancies of the spectral lines of the simple substances vary under different temperatures and pressures; so that all probabilities are in favour of the helium line simply belonging to some long since known element placed under such conditions of temperature, pressure, and gravity as have not yet been realised in our experiments. Again, the idea that the excellent investigations of Lockyer of the spectrum of iron can be interpreted in favour of the compound nature of that element, evidently must have arisen from some misunderstanding. The spectrum of a compound certainly does not appear as a sum of the spectra of its components; and therefore the observations of Lockyer can be considered precisely as a proof that iron undergoes no other changes at the temperature of the sun than those which it experiences in the voltaic arc—provided the spectrum of iron is preserved. As to the shifting of some of the lines of the spectrum of iron while the other lines maintain their positions, it can be explained, as shown by M. Kleiber ('Journal of the Russian Chemical and Physical Society, 1885, 147), by the relative motion of the various strata of the sun's atmosphere, and by Zöllner's laws of the relative brilliancies of different lines of the spectrum. Moreover, it ought not to be forgotten that if iron were really proved to consist of two or more unknown elements, we should simply have an increase in the number of our elements—not a reduction, and still less a reduction of all of them to one single primary matter.

Feeling that spectrum analysis will not yield a support to the Pythagorean conception, its modern promoters are so bent upon its being confirmed by the periodic law, that the illustrious Berthelot, in his work 'Les origines de l'Alchimie,' 1885, 313, has simply mixed up the fundamental idea of the law of periodicity with the ideas of Prout, the alchemists, and Democritus about primary matter.[4] But the periodic law, based as it is on the solid and whole-some ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of a unique matter; and it has no historical connection with that relic of the torments of classical thought, and therefore it affords no more indication of the unity of matter or of the compound character of our elements, than the law of Avogadro, or the law of specific heats, or even the conclusions of spectrum analysis. None of the advocates of a unique matter have ever tried to explain the law from the standpoint of ideas taken from a remote antiquity when it was found convenient to admit the existence of many gods—and of a unique matter.

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[3] That is, a substance having a wave-length equal to 0·0005875 millimetre.

[4] He maintains (on p. 309) that the periodic law requires two new analogous elements, having atomic weights of 48 and 64, occupying positions between sulphur

When we try to explain the origin of the idea of a unique primary matter, we easily trace that in the absence of inductions from experiment it derives its origin from the scientifically philosophical attempt at discovering some kind of unity in the immense diversity of individualities which we see around. In classical times such a tendency could only be satisfied by conceptions about the immaterial world. As to the material world, our ancestors were compelled to resort to some hypothesis, and they adopted the idea of unity in the formative material, because they were not able to evolve the conception of any other possible unity in order to connect the multifarious relations of matter. Responding to the same legitimate scientific tendency, natural science has discovered throughout the universe a unity of plan, a unity of forces, and a unity of matter, and the convincing conclusions of modern science compel every one to admit these kinds of unity. But while we admit unity in many things, we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere. It has been said of old, 'Give us a fulcrum, and it will become easy to displace the earth.' So also we must say, 'Give us something that is individualised, and the apparent diversity will be easily understood.' Otherwise, how could unity result in a multitude?

After a long and painstaking research, natural science has discovered the individualities of the chemical elements, and therefore it is now capable not only of analysing, but also of synthesising; it can understand and grasp generality and unity, as well as the individualised and the multifarious. The general and universal, like time and space, like force and motion, vary uniformly; the uniform admit of interpolations, revealing every intermediate phase. But the multitudinous, the individualised—such as ourselves, or the chemical elements, or the members of a peculiar periodic function of the elements, or Dalton's multiple proportions—is characterised in another way: we see in it, side by side with a connecting general principle, leaps, breaks of continuity, points which escape from the analysis of the infinitely small—an absence of complete intermediate links. Chemistry has found an answer to the question as to the causes of multitudes; and while retaining the conception of many elements, all submitted to the discipline of a general law, it offers an escape from the Indian Nirvana—the absorption in the universal, replacing it by the individualised. However, the place for indi-

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and selenium, although nothing of the kind results from any of the different readings of viduality is so limited by the all-grasping, all-powerful universal, that merely a point of support for the understanding of multitude in unity.

Having touched upon the metaphysical bases of the conception unique matter which is supposed to enter into the composition of all bo I think it necessary to dwell upon another theory, akin to the above con tion—the theory of the compound character of the elements now admitte some—and especially upon one particular circumstance which, being re to the periodic law, is considered to be an argument in favour of that h thesis.

Dr. Pelopidas, in 1883, made a communication to the Russian Cher and Physical Society on the periodicity of the hydrocarbon radicles, poi out the remarkable parallelism which was to be noticed in the chan properties of hydrocarbon radicles and elements when classed in gr Professor Carnelley, in 1886, developed a similar parallelism. The id M. Pelopidas will be easily understood if we consider the series of hy carbon radicles which contain, say, 6 atoms of carbon :—

I.	II.	III.	IV.	V.	VI.	VII.
C_6H_{13}	C_6H_{12}	C_6H_{11}	C_6H_{10}	C_6H_9	C_6H_8	C_6H_7

The first of these radicles, like the elements of the 1st group, combines Cl, OH, and so on, and gives the derivatives of hexyl alcohol, C_6H_{13}(C but, in proportion as the number of hydrogen atoms decreases, the cap of the radicles of combining with, say, the halogens increases. C_6H_{12} alr combines with 2 atoms of chlorine; C_6H_{11} with 3 atoms, and so on. last members of the series comprise the radicles of acids: thus C_6H_8, w belongs to the 6th group, gives, like sulphur, a bibasic acid, $C_6H_8O_2$(C which is homologous with oxalic acid. The parallelism can be traced further, because C_6H_5 appears as a monovalent radicle of benzene, and it begins a new series of aromatic derivatives, so analogous to the derivati the aliphatic series. Let me also mention another example from among which have been given by M. Pelopidas. Starting from the alkaline ra of monomethylammonium, $N(CH_3)H_3$, or NCH_6, which presents r analogies with the alkaline metals of the 1st group, he arrives, by success diminishing the number of the atoms of hydrogen, at a 7th group w contains cyanogen, CN, which has long since been compared to the halo of the 7th group.

The most important consequence which, in my opinion, can be d from the above comparison is that the periodic law, so apparent in elements, has a wider application than might appear at first sight; it o up a new vista of chemical evolutions. But, while admitting the fu parallelism between the periodicity of the elements and that of the comp radicles, we must not forget that in the periods of the hydrocarbon rad we have a *decrease* of mass as we pass from the representatives of the group to the next, while in the periods of the elements the mass *incr* during the progression. It thus becomes evident that we cannot speak identity of periodicity in both cases, unless we put aside the ideas of and attraction, which are the real corner-stones of the whole of na science, and even enter into those very conceptions of simple substances w came to light a full hundred years later than the immortal principles of Newton.[5]

From the foregoing, as well as from the failures of so many attempts at finding in experiment and speculation a proof of the compound character of the elements and of the existence of primordial matter, it is evident, in my opinion, that this theory must be classed among mere utopias. But utopias can only be combated by freedom of opinion, by experiment, and by new utopias. In the republic of scientific theories freedom of opinions is guaranteed. It is precisely that freedom which permits me to criticise openly the widely-diffused idea as to the unity of matter in the elements. Experiments and attempts at confirming that idea have been so numerous that it really would be instructive to have them all collected together, if only to serve as a warning against the repetition of old failures. And now as to new utopias which may be helpful in the struggle against the old ones, I do not think it quite useless to mention a *phantasy* of one of my students who imagined that the weight of bodies does not depend upon their mass, but upon the character of the motion of their atoms. The atoms, according to this new utopian, may all be homogeneous or heterogeneous, we know not which; we know them in motion only, and that motion they maintain with the same persistence as the stellar bodies maintain theirs. The weights of atoms differ only in consequence of their various modes and quantity of motion; the heaviest atoms may be much simpler than the lighter ones: thus an atom of mercury may be simpler than an atom of hydrogen—the manner in which it moves causes it to be heavier. My interlocutor even suggested that the view which attributes the greater complexity to the lighter elements finds confirmation in the fact that the hydrocarbon radicles mentioned by Pelopidas, while becoming lighter as they lose hydrogen, change their properties periodically in the same manner as the elements change theirs, according as the atoms grow heavier.

The French proverb, *La critique est facile, mais l'art est difficile*, however, may well be reversed in the case of all such ideal views, as it is much easier to formulate than to criticise them. Arising from the virgin soil of newly-established facts, the knowledge relating to the elements, to their masses, and to the periodic changes of their properties has given a motive for the formation of utopian hypotheses, probably because they could not be foreseen by the aid of any of the various metaphysical systems, and exist, like the idea of gravitation, as an independent outcome of natural science, requiring the acknowledgment of general laws, when these have been established with the same degree of persistency as is indispensable for the acceptance of a thoroughly established fact. Two centuries have elapsed since the theory of gravitation was enunciated, and although we do not understand its cause, we still must regard gravitation as a fundamental conception of natural philosophy, a conception which has enabled us to perceive much more than the metaphysicians did or could with their seeming omniscience. A hundred

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[5] It is noteworthy that the year in which Lavoisier was born (1743)—the author of the idea of elements and of the indestructibility of matter—is later by exactly one century than the year in which the author of the theory of gravitation and mass was born

years later the conception of the elements arose; it made chemistry wh
now is; and yet we have advanced as little in our comprehension of si
substances since the times of Lavoisier and Dalton as we have in our u
standing of gravitation. The periodic law of the elements is only tw
years old; it is not surprising, therefore, that, knowing nothing about
causes of gravitation and mass, or about the nature of the elements, w
not comprehend the *rationale* of the periodic law. It is only by colle
established laws—that is, by working at the acquirement of truth—tha
can hope gradually to lift the veil which conceals from us the causes o
mysteries of Nature and to discover their mutual dependency. Like
telescope and the microscope, laws founded on the basis of experimen
the instruments and means of enlarging our mental horizon.

In the remaining part of my communication I shall endeavour to s
and as briefly as possible, in how far the periodic law contributes to en
our range of vision. Before the promulgation of this law the che
elements were mere fragmentary, incidental facts in Nature; there w
special reason to expect the discovery of new elements, and the new
which were discovered from time to time appeared to be possessed of
novel properties. The law of periodicity first enabled us to perceive u
covered elements at a distance which formerly was inaccessible to che
vision; and long ere they were discovered new elements appeared befor
eyes possessed of a number of well-defined properties. We now know
cases of elements whose existence and properties were foreseen by the in
mentality of the periodic law. I need but mention the brilliant discove
gallium, which proved to correspond to eka-aluminium of the periodic la
Lecoq de Boisbaudran; of *scandium*, corresponding to ekaboron, by Ni
and of *germanium*, which proved to correspond in all respects to ekasi
by Winkler. When, in 1871, I described to the Russian Chemical So
the properties, clearly defined by the periodic law, which such ele
ought to possess, I never hoped that I should live to mention their disc
to the Chemical Society of Great Britain as a confirmation of the exac
and the generality of the periodic law. Now that I have had the hap
of doing so, I unhesitatingly say that, although greatly enlarging our v
even now the periodic law needs further improvements in order that it
become a trustworthy instrument in further discoveries.[6]

I will venture to allude to some other matters which chemistry ha
cerned by means of its new instrument, and which it could not have

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[6] I foresee some more new elements, but not with the same certitude as befo
shall give one example, and yet I do not see it quite distinctly. In the series whic
tains Hg = 204, Pb = 206, and Bi = 208, we can imagine the existence (at the place V
of an element analogous to tellurium, which we can describe as dvi-tellurium, Dt,
an atomic weight of 212, and the property of forming the oxide DtO_3. If this el
really exists, it ought in the free state to be an easily fusible, crystalline, non-v
metal of a grey colour, having a density of about 9·3, capable of giving a dioxide,
equally endowed with feeble acid and basic properties. This dioxide must give on
oxidation an unstable higher oxide, DtO_3, which should resemble in its properties
and Bi_2O_5. Dvi-tellurium hydride, if it be found to exist, will be a less stable com
than even H_2Te. The compounds of dvi-tellurium will be easily reduced, and it wi
characteristic definite alloys with other metals.

out without a knowledge of the law of periodicity, and I will confine myself to simple substances and to oxides.

Before the periodic law was formulated the atomic weights of the elements were purely empirical numbers, so that the magnitude of the equivalent, and the atomicity, or the value in substitution possessed by an atom, could only be tested by critically examining the methods of determination, but never directly by considering the numerical values themselves; in short, we were compelled to move in the dark, to submit to the facts, instead of being masters of them. I need not recount the methods which permitted the periodic law at last to master the facts relating to atomic weights, and I would merely call to mind that it compelled us to modify the valencies of *indium* and *cerium*, and to assign to their compounds a different molecular composition. Determinations of the specific heats of these two metals fully confirmed the change. The trivalency of *yttrium*, which makes us now represent its oxide as Y_2O_3 instead of as YO, was also foreseen (in 1870) by the periodic law, and it has now become so probable that Clève, and all other subsequent investigators of the rare metals, have not only adopted it, but have also applied it without any new demonstration to substances so imperfectly known as those of the cerite and gadolinite group, especially since Hillebrand determined the specific heats of lanthanum and didymium and confirmed the expectations suggested by the periodic law. But here, especially in the case of didymium, we meet with a series of difficulties long since foreseen through the periodic law, but only now becoming evident, and chiefly arising from the relative rarity and insufficient knowledge of the elements which usually accompany didymium.

Passing to the results obtained in the case of the rare elements *beryllium*, *scandium*, and *thorium*, it is found that these have many points of contact with the periodic law. Although Avdéeff long since proposed the magnesia formula to represent beryllium oxide, yet there was so much to be said in favour of the alumina formula, on account of the specific heat of the metals and the isomorphism of the two oxides, that it became generally adopted and seemed to be well established. The periodic law, however, as Brauner repeatedly insisted ('Berichte,' 1878, 872; 1881, 58), was against the formula Be_2O_3; it required the magnesia formula BeO—that is, an atomic weight of 9—because there was no place in the system for an element like beryllium having an atomic weight of 13·5. This divergence of opinion lasted for years, and I often heard that the question as to the atomic weight of beryllium threatened to disturb the generality of the periodic law, or, at any rate, to require some important modifications of it. Many forces were operating in the controversy regarding beryllium, evidently because a much more important question was at issue than merely that involved in the discussion of the atomic weight of a relatively rare element: and during the controversy the periodic law became better understood, and the mutual relations of the elements became more apparent than ever before. It is most remarkable that the victory of the periodic law was won by the researches of the very observers who previously had discovered a number of facts in support of the trivalency of beryllium. Applying the higher law of Avogadro, Nilson and Pettersson have finally shown that the density of the vapour of the beryllium chloride, $BeCl_2$, obliges us to regard beryllium as bivalent in conformity with the periodic law.[7] I consider the confirmation of Avdéeff's and Brauner's view as important in the history of the periodic law as the discovery of scandium, which, in Nilson's hands, confirmed the existence of ekaboron.

The circumstance that *thorium* proved to be quadrivalent, and Th = 232, in accordance with the views of Chydenius and the requirements of the periodic law, passed almost unnoticed, and was accepted without opposition, and yet both thorium and uranium are of great importance in the periodic system, as they are its last members, and have the highest atomic weights of all the elements.

The alteration of the atomic weight of *uranium* from U = 120 into U = 240 attracted more attention, the change having been made on account of the periodic law, and for no other reason. Now that Roscoe, Rammelsberg, Zimmermann, and several others have admitted the various claims of the periodic law in the case of uranium, its high atomic weight is received without objection, and it endows that element with a special interest.

While thus demonstrating the necessity for modifying the atomic weights of several insufficiently known elements, the periodic law enabled us also to detect errors in the determination of the atomic weights of several elements whose valencies and true position among other elements were already well known. Three such cases are especially noteworthy: those of tellurium, titanium and platinum. Berzelius had determined the atomic weight of *tellurium* to be 128, while the periodic law claimed for it an atomic weight below that of iodine, which had been fixed by Stas at 126·5, and which was certainly not higher than 127. Brauner then undertook the investigation, and he has shown that the true atomic weight of tellurium is lower than that of iodine, being near to 125. For *titanium* the extensive researches of Thorpe have confirmed the atomic weight of Ti = 48, indicated by the law, and already foreseen by Rose, but contradicted by the analyses of Pierre and several other chemists. An equally brilliant confirmation of the expectations based on the periodic law has been given in the case of the series osmium, iridium, platinum, and gold. At the time of the promulgation of the periodic law, the determinations of Berzelius, Rose, and many others gave the following figures:—

Os = 200; Ir = 197; Pt = 198; Au = 196.

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[7] Let me mention another proof of the bivalency of beryllium which may have passed unnoticed, as it was only published in the Russian chemical literature. Having remarked (in 1884) that the density of such solutions of chlorides of metals, MCl_n, as contain 200 mols. of water (or a large and constant amount of water) regularly increases as the molecular weight of the dissolved salt increases, I proposed to one of our young chemists, M. Burdakoff, that he should investigate beryllium chloride. If its molecule be $BeCl_2$ its weight must be = 80; and in such a case it must be heavier than the molecule of KCl = 74·5, and lighter than that of $MgCl_2$ = 95. On the contrary, if beryllium chloride is a trichloride, $BeCl_3$ = 120, its molecule must be heavier than that of $CaCl_2$ = 111, and lighter than that of $MnCl_2$ = 126. Experiment has shown the correctness of the former formula, the solution $BeCl_2 + 200H_2O$ having (at 15°/4°) a density of 1·0188, this being a higher density than that of the solution $KCl + 200H_2O$ (= 1·0121), and lower than that of $MgCl_2 + 200H_2O$ (= 1·0208). The bivalency of beryllium was thus confirmed in the case both of the dissolved and the vaporised chloride.

The expectations of the periodic law[8] have been confirmed, first, by new determinations of the atomic weight of *platinum* (by Seubert, Dittmar, and M'Arthur, which proved to be near to 196 (taking O = 16, as proposed by Marignac, Brauner, and others); secondly, by Seubert having proved that the atomic weight of *osmium* is really lower than that of platinum, being near to 191; and thirdly, by the investigations of Krüss, Thorpe and Laurie, proving that the atomic weight of *gold* exceeds that of platinum, and approximates to 197. The atomic weights which were thus found to require correction were precisely those which the periodic law had indicated as affected with errors; and it has been proved, therefore, that the periodic law affords a means of testing experimental results. If we succeed in discovering the exact character of the periodic relationships between the increments in atomic weights of allied elements discussed by Rydberg in 1885, and again by Bazaroff in 1887, we may expect that our instrument will give us the means of still more closely controlling the experimental data relating to atomic weights.

Let me next call to mind that, while disclosing the variation of chemical properties,[9] the periodic law has also enabled us to systematically discuss many of the physical properties of elementary bodies, and to show that these properties are also subject to the law of periodicity. At the Moscow Congress of Russian Naturalists in August, 1869, I dwelt upon the relations which existed between density and the atomic weight of the elements. The following year Professor Lothar Meyer, in his well-known paper,[10] studied the same subject in more detail, and thus contributed to spread information about the periodic law. Later on, Carnelley, Laurie, L. Meyer, Roberts-Austen, and several others applied the periodic system to represent the order in the changes of the magnetic properties of the elements, their melting points, the heats of formation of their haloid compounds, and even of such mechanical properties as the co-efficient of elasticity, the breaking stress, &c., &c. These deductions, which have received further support in the discovery of new elements endowed not only with chemical but even with physical properties, which were foreseen by the law of periodicity, are well known; so I need not dwell upon the subject, and may pass to the consideration of oxides.[11]

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[8] I pointed them out in the *Liebig's Annalen*, Supplement Band., viii. 1871, p. 211.

[9] Thus, in the typical small period of

Li, Be, B, C, N, O, F,

we see at once the progression from the alkali metals to the acid non-metals, such as are the halogens.

[10] *Liebig's Annalen*, Supplement Band., vii. 1870.

[11] A distinct periodicity can also be discovered in the spectra of the elements. Thus the researches of Hartley, Ciamician, and others have disclosed, first, the homology of the spectra of analogous elements; secondly, that the alkali metals have simpler spectra than the metals of the following groups; and thirdly, that there is a certain likeness between the complicated spectra of manganese and iron on the one hand, and the no less complicated spectra of chlorine and bromine on the other hand, and their likeness corresponds to the degree of analogy between those elements which is indicated by the

In indicating that the gradual increase of the power of elements of combining with oxygen is accompanied by a corresponding decrease in their power of combining with hydrogen, the periodic law has shown that there is a limit of oxidation, just as there is a well-known limit to the capacity of elements for combining with hydrogen. A single atom of an element combines with at most four atoms of either hydrogen or oxygen; and while CH_4 and SiH_4 represent the highest hydrides, so RuO_4 and OsO_4 are the highest oxides. We are thus led to recognise types of oxides, just as we have had to recognise types of hydrides.[12]

The periodic law has demonstrated that the maximum extent to which different non-metals enter into combination with oxygen is determined by the extent to which they combine with hydrogen, and that the sum of the number of equivalents of both must be equal to 8. Thus chlorine, which combines with 1 atom or 1 equivalent of hydrogen, cannot fix more than 7 equivalents of oxygen, giving Cl_2O_7; while sulphur, which fixes 2 equivalents of hydrogen, cannot combine with more than 6 equivalents or 3 atoms of oxygen. It thus becomes evident that we cannot recognise as a fundamental property of the elements the atomic valencies deduced from their hydrides; and that we must modify, to a certain extent, the theory of atomicity if we desire to raise it to the dignity of a general principle capable of affording an insight into the constitution of all compound molecules. In other words, it is only to carbon, which is quadrivalent with regard both to oxygen and hydrogen, that we can apply the theory of constant valency and of bond, by means of which so many still endeavour to explain the structure of compound molecules. But I should go too far if I ventured to explain in detail the conclusions which can be drawn from the above considerations. Still, I think it necessary to dwell upon one particular fact which must be explained from the point of view of the periodic law in order to clear the way to its extension in that particular direction.

The higher oxides yielding salts the formation of which was foreseen by the periodic system—for instance, in the short series beginning with sodium—

$$Na_2O,\ MgO,\ Al_2O_3,\ SiO_2,\ P_2O_5,\ SO_3,\ Cl_2O_7,$$

must be clearly distinguished from the higher degrees of oxidation which correspond to hydrogen peroxide and bear the true character of peroxides. Peroxides such as Na_2O_2, BaO_2, and the like have long been known. Similar

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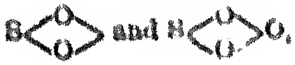
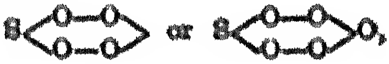
[12] Formerly it was supposed that, being a bivalent element, oxygen can enter into any grouping of the atoms, and there was no limit foreseen as to the extent to which it could further enter into combination. We could not explain why bivalent sulphur, which forms compounds such as



could not also form oxides such as—



while other elements, as, for instance, chlorine, form compounds such as—

peroxides have also recently become known in the case of chromium, sulphur, titanium, and many other elements, and I have sometimes heard it said that discoveries of this kind weaken the conclusions of the periodic law in so far as it concerns the oxides. I do not think so in the least, and I may remark, in the first place, that all these peroxides are endowed with certain properties obviously common to all of them, which distinguish them from the actual, higher, salt-forming oxides, especially their easy decomposition by means of simple contact agencies; their incapability of forming salts of the common type; and their capability of combining with other peroxides (like the faculty which hydrogen peroxide possesses of combining with barium peroxide, discovered by Schoene). Again, we remark that some groups are especially characterised by their capacity of generating peroxides. Such is, for instance, the case in the sixth group, where we find the well-known peroxides of sulphur, chromium, and uranium; so that further investigation of peroxides will probably establish a new periodic function, foreshadowing that molybdenum and tungsten will assume peroxide forms with comparative readiness. To appreciate the constitution of such peroxides, it is enough to notice that the peroxide form of sulphur (so-called persulphuric acid) stands in the same relation to sulphuric acid as hydrogen peroxide stands to water:—

$H(OH)$, or H_2O, responds to $(OH)(OH)$, or H_2O_2,

and so also—

$H(HSO_4)$, or H_2SO_4, responds to $(HSO_4)(HSO_4)$, or $H_2S_2O_8$.

Similar relations are seen everywhere, and they correspond to the principle of substitutions which I long since endeavoured to represent as one of the chemical generalisations called into life by the periodic law. So also sulphuric acid, if considered with reference to hydroxyl, and represented as follows—

$HO(SO_2OH)$,

has its corresponding compound in dithionic acid—

$(SO_2OH)(SO_2OH)$, or $H_2S_2O_6$.

Therefore, also, phosphoric acid, $HO(POH_2O_2)$, has, in the same sense, its corresponding compound in the subphosphoric acid of Salzer:—

$(POH_2O_2)(POH_2O_2)$, or $H_4P_2O_6$;

and we must suppose that the peroxide compound corresponding to phosphoric acid, if it be discovered, will have the following structure:—

$(H_2PO_4)_2$ or $H_4P_2O_8 = 2H_2O + 2PO_3$.[13]

So far as is known at present, the highest form of peroxides is met with in the peroxide of uranium, UO_4, prepared by Fairley;[14] while OsO_4 is the highest oxide giving salts. The line of argument which is inspired by the periodic law, so far from being weakened by the discovery of peroxides, is thus actually strengthened, and we must hope that a further exploration of the region under consideration will confirm the applicability to chemistry generally of the principles deduced from the periodic law.

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[13] In this sense, oxalic acid, $(COOH)_2$, also corresponds to carbonic acid, $OH(COOH)$, in the same way that dithionic acid corresponds to sulphuric acid, and subphosphoric acid to phosphoric; hence, if a peroxide corresponding to carbonic acid be obtained, it will have the structure of $(HCO_3)_2$, or $H_2C_2O_6 = H_2O + C_2O_5$. So also lead must have a real peroxide, Pb_2O_5.

Permit me now to conclude my rapid sketch of the oxygen compounds by the observation that the periodic law is especially brought into evidence in the case of the oxides which constitute the immense majority of bodies at our disposal on the surface of the earth.

The oxides are evidently subject to the law, both as regards their chemical and their physical properties, especially if we take into account the cases of polymerism which are so obvious when comparing CO_2 with Si_nO_{2n}. In order to prove this I give the densities *s* and the specific volumes *v* of the higher oxides of two short periods. To render comparison easier, the oxides are all represented as of the form R_2O_n. In the column headed Δ the differences are given between the volume of the oxygen compound and that of the parent element, divided by *n*—that is, by the number of atoms of oxygen in the compound:—[15]

	s.	*v.*	Δ		*s.*	*v.*	Δ
Na_2O	2·6	24	−22	K_2O	2·7	35	−55
Mg_2O_2	3·6	22	−3	Ca_2O	3·15	36	−7
Al_2O_3	4·0	26	+1·3	Sc_2O_3	3·86	35	0
Si_2O_4	2·65	45	5·2	Li_2O_4	4·2	38	+5
P_2O_5	2·39	59	6·2	V_2O_5	3·49	52	6·7
S_2O_6	1·96	82	8·7	Cr_2O_6	2·74	73	9·5

I have nothing to add to these figures, except that like relations appear in other periods as well. The above relations were precisely those which made it possible for me to be certain that the relative density of ekasilicon oxide would be about 4·7; germanium oxide, actually obtained by Winkler, proved, in fact, to have the relative density 4·703.

The foregoing account is far from being an exhaustive one of all that has already been discovered by means of the periodic law telescope in the boundless realms of chemical evolution. Still less is it an exhaustive account of all that may yet be seen, but I trust that the little which I have said will account for the philosophical interest attached in chemistry to this law. Although but a recent scientific generalisation, it has already stood the test of laboratory verification, and appears as an instrument of thought which has not yet been compelled to undergo modification; but it needs not only new applications, but also improvements, further development, and plenty of fresh energy. All this will surely come, seeing that such an assembly of men of science as the Chemical Society of Great Britain has expressed the desire to have the history of the periodic law described in a lecture dedicated to the glorious name of Faraday.

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[14] The compounds of uranium prepared by Fairley seem to me especially instructive in understanding the peroxides. By the action of hydrogen peroxide on uranium oxide, UO_3, a peroxide of uranium, $UO_4,4H_2O$, is obtained ($U=240$) if the solution be acid; but if hydrogen peroxide act on uranium oxide in the presence of caustic soda, a crystalline deposit is obtained which has the composition $Na_4UO_8,4H_2O$, and evidently is a combination of sodium peroxide, Na_2O_2, with uranium peroxide, UO_4. It is possible that the former peroxide, $UO_4,4H_2O$, contains the elements of hydrogen peroxide and uranium peroxide, U_2O_7, or even $U(OH)_6,H_2O_2$, like the peroxide of tin recently discovered by Spring, which has the constitution Sn_2O_5,H_2O_2.

[15] Δ thus represents the average increase of volume for each atom of oxygen contained in the higher salt-forming oxide. The acid oxides give, as a rule, a higher value

APPENDIX III

ARGON, A NEW CONSTITUENT OF THE ATMOSPHERE.

WRITTEN BY PROFESSOR MENDELÉEFF IN FEBRUARY 1895.

THE remarks made in Chapter V., Note 16 bis respecting the newly discovered constituent of the atmosphere are here supplemented by data (taken from the publications of the Royal Society of London) given by the discoverers Lord Rayleigh and Professor Ramsay in January 1895, together with observations made by Crookes and Olszewsky upon the same subject.

This gas, which was discovered by Rayleigh and Ramsay in atmospheric nitrogen, was named *argon*[1] by them, and upon the supposition of its being an element, they gave it the symbol A. But its true chemical nature is not yet fully known, for not only has no compound of it been yet obtained, but it has not even been brought into any reaction. From all that is known about it at the present time, we may conclude with the discoverers that argon belongs to those gases which are permanent constituents of the atmosphere, and that it is a new element. The latter statement, however, requires confirmation. We shall presently see, however, that the negative chemical character of argon (its incapacity to react with any substance), and the small amount of it present in the atmosphere (about 1¼ per cent. by volume in the nitrogen of air, and consequently about 1 per cent. by volume in air), as well as the recent date of its discovery (1894) and the difficulty of its preparation, are quite sufficient reasons for the incompleteness of the existing knowledge respecting this element. But since, so far as is yet known, we are dealing with a normal constituent of the atmosphere[1 bis], the

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[1] From the Greek Αργὸν—inert.

[1 bis] In Note 16 bis, Chapter V., I mentioned that, judging from the specific gravity of argon, it might possibly be polymerised nitrogen, N_3, bearing the same relationship to nitrogen, N_2, that ozone, O_3, bears to ordinary oxygen. If this idea were confirmed, still one would not imagine that argon was formed from the atmospheric nitrogen by those reactions by which it was obtained by Rayleigh and Ramsay, but rather that it arises from the nitrogen of the atmosphere under natural conditions. Although this proposition is not quite destroyed by the more recent results, still it is contradicted by the fact that

existing data, notwithstanding their insufficiently definite nature, should find a place even in such an elementary work as the present, all the more as the names of Rayleigh, Ramsay, Crookes and Olszewsky, who have worked upon argon, are among the highest in our science, and their researches among the most difficult.[2] These researches, moreover, were directed straight to the goal, which was only partly reached owing to the unusual properties of argon itself.

When it became known (Chapter V., Note 4 bis) that the nitrogen obtained from air (by removing the oxygen, moisture and CO_2 by various reagents) has a greater density than that obtained from the various (oxygen, hydrogen and metallic) compounds of nitrogen, it was a plausible explanation that the latter contained an admixture of hydrogen, or of some other light gas lowering the density of the mixture. But such an assumption is refuted not only by the fact that the nitrogen obtained from its various compounds (after purification) has always the same density (although the supposed impurities mixed with it should vary), but also by Rayleigh and Ramsay's experiment of artificially adding hydrogen to nitrogen, and then passing the mixture over red-hot oxide of copper, when it was found that the nitrogen regained its original density, *i.e.* that the whole of the hydrogen was removed by this treatment. Therefore the difference in the density of the two varieties of nitrogen had to be explained by the presence of a heavier gas in admixture with the nitrogen obtained from the atmosphere. This hypothesis was confirmed by the fact that Rayleigh and Ramsay having obtained purified nitrogen (by removing the O_2, CO_2 and H_2O), both from ordinary air and from air which had been previously subjected to atmolysis, that is which had been passed through porous tubes (of burnt clay, *e.g.* pipe-stem), surrounded by a rarefied space, and so deprived of its lighter constituents (chiefly nitrogen), found that the nitrogen from the air which had been subjected to atmolysis was heavier than that obtained from air which had not been so treated. This experiment showed that the nitrogen of air contains an admixture of a gas which, being heavier than nitrogen itself,[3] diffuses more slowly than nitrogen

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to subject it to as high a temperature as possible. And the possibility of nitrogen polymerising is all the more admissible from the fact that the aggregation of its atoms in the molecule is not at all unlikely, and that polymerised nitrogen, judging from many examples, might be inert if the polymerisation were accompanied by the evolution of heat. In the following footnotes I frequently return to this hypothesis, not only because I have not yet met any facts definitely contradictory to it, but also because the chief properties of argon agree with it to a certain extent.

[2] The chief difficulty in investigating argon lies in the fact that its preparation requires the employment of a large quantity of air, which has to be treated with a number of different reagents, whose perfect purity (especially that of magnesium) will always be doubtful, and argon has not yet been transferred to a substance in which it could be easily purified. Perhaps the considerable solubility of argon in water (or in other suitable liquids, which have not apparently yet been tried) may give the means of doing so, and it may be possible, by collecting the air expelled from boiling water, to obtain a richer source of argon than ordinary air.

[3] It might also be supposed that this heavy gas is separated by the copper when the latter absorbs the oxygen of the air; but such a supposition is not only improbable in

through the porous material. It remained, therefore, to separate this impurity from the nitrogen. To do this Rayleigh and Ramsay adopted two methods, converting the nitrogen into solid and liquid substances, either by absorbing the nitrogen by heated magnesium (Chapter V., Note 6, and Chapter XIV., Note 14), with the formation of nitride of magnesium, or else by converting it into nitric acid by the action of electric sparks or the presence of an excess of air and alkali, as in Cavendish's method.[3 bis] In both cases the nitrogen entered into reaction, while the heavier gas mixed with it remained inert, and was thus able to be isolated. That is, the argon could be separated by these means from the excess of atmospheric nitrogen accompanying it.[4] As an illustration we will describe how argon was obtained from the atmospheric nitrogen by means of magnesium.[5] To begin with, it was discovered that when atmospheric nitrogen was passed through a tube containing metallic magnesium heated to redness, its specific gravity rose to 14·88. As this showed that part of the gas was absorbed by the magnesium, a mercury gasometer filled with atmospheric nitrogen was taken, and the gas drawn over soda-lime, P_2O_5, heated magnesium[6] and then through tubes containing red-hot copper oxide, soda-lime and phosphoric anhydride to a second mercury gasometer. Every time the gas was repassed through the tubes, it decreased in volume and increased in density. After repeating

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of the metals, like FeO) besides red-hot copper, and that the nitrogen obtained is always just as heavy. Besides which, nitrogen is also set free from its oxides by copper, and the nitrogen thus obtained is lighter. Therefore it is not the copper which produces the heavy gas—*i.e.* argon.

[3 bis] It is worthy of note that Cavendish obtained a small residue of gas in converting nitrogen into nitric acid; but he paid no attention to it, although probably he had in his hands the very argon recently discovered.

[4] When in these experiments, instead of atmospheric nitrogen the gas obtained from its compound was taken, an inert residue of a heavy gas, having the properties of argon, was also remarked, but its amount was very small. Rayleigh and Ramsay ascribe the formation of this residue to the fact that the gas in these experiments was collected over water, and a portion of the dissolved argon in it might have passed into the nitrogen. As the authors of this supposition did not prove it by any special experiments, it forms a weak point in their classical research. If it be admitted that argon is N_3, the fact of its being obtained from the nitrogen of compounds might be explained by the polymerisation of a portion of the nitrogen in the act of reaction, although it is impossible to refute Rayleigh and Ramsay's hypothesis of its being evolved from the water employed in the manipulation of the gases. Three thousand volumes of nitrogen extracted from its compounds gave about three volumes of argon, while thirty volumes were yielded by the same amount of atmospheric nitrogen.

[5] The preparation of argon by the conversion of nitrogen into nitric acid is complicated by the necessity of adding a large proportion of oxygen and alkali, of passing an electric discharge through the mixture for a long period, and then removing the remaining oxygen. All this was repeatedly done by the authors, but this method is far more complex, both in practice and theory, than the preparation of argon by means of magnesium. From 100 volumes of air subjected to conversion into HNO_3, 0·76 volume of argon were obtained after absorbing the excess of oxygen.

[6] In these and the following experiments the magnesium was placed in an ordinary hard glass tube, and heated in a gas furnace to a temperature almost sufficient to soften the glass. The current of gas must be very slow (a tube containing a small quantity of sulphuric acid served as a meter), as otherwise the heat evolved in the formation of the

this for ten days 1,500 c.c. of gas were reduced to 200 cc., and the density increased to 16·1 (if that of $H_2 = 1$ and $N_2 = 14$). Further treatment of the remainder brought the density up to 19·09. After adding a small quantity of oxygen and repassing the gas through the apparatus, the density rose to 20·0. To obtain argon by this process Ramsay and Rayleigh (employing a mercury air pump and mercury gasometers) once treated about 150 litres of atmospheric nitrogen. On another occasion they treated 7,925 c.c. of air by the oxidation method and obtained 65 c.c. of argon, which corresponds to 0·82 per cent. The density of the argon obtained by this means was nearly 19·7, while that obtained by the magnesium method varied between 19·09 and 20·88.

Thus the first positive and very important fact respecting argon is that its specific gravity is nearly 20—that is, that it is 20 times heavier than hydrogen, while nitrogen is only 14 times and oxygen 16 times heavier than hydrogen. This explains the difference observed by Rayleigh between the densities of nitrogen obtained from its compounds and from the atmosphere (Chapter V., Note 4 bis). At 0° and 760 mm. a litre of the former gas weighs 1·2505 grm., while a litre of the latter weighs 1·2572, or taking H = 1, the density of the first = 13·916, and of the latter = 13·991. If the density of argon be taken as 20, it is contained in atmospheric nitrogen to the extent of about 1·23 per cent. by volume, whilst air contains about 0·97 per cent. by volume.

When argon had been isolated the question naturally arose, was it a new homogeneous substance having definite properties or was it a mixture of gases? The former may now be positively asserted, namely, that argon is a peculiar gas previously unknown to chemistry. Such a conviction is in the first place established by the fact that argon has a greater number of negative properties, a smaller capacity for reaction, than any other simple or compound body known. The most inert gas known is nitrogen, but argon far exceeds it in this respect. Thus nitrogen is absorbed at a red heat by many metals, with the formation of nitrides, while argon, as is seen in the mode of its preparation and by direct experiment, does not possess this property. Nitrogen, under the action of electric sparks, combines with hydrogen in the presence of acids and with oxygen in the presence of alkalis, while argon is unable to do so, as is seen from the method of separation from nitrogen. Rayleigh and Ramsay also proved that argon is unable to react with chlorine (dry or moist) either directly or under the action of an electric discharge, or with phosphorus or sulphur, at a red heat. Sodium, potassium, and tellurium may be distilled in an atmosphere of argon without change. Fused caustic soda, incandescent soda-lime, molten nitre, red-hot peroxide of sodium, and the polysulphides of calcium and sodium also do not react with argon. Platinum black does not absorb it, and spongy platinum is unable to excite its reaction with oxygen or chlorine. Aqua regia, bromine water, and a mixture of hydrochloric acid and $KMnO_4$ were also without action upon argon. Besides which it is evident from the method of its preparation that it is not acted upon by red-hot oxide of copper. All these facts exclude any possibility of argon con-

confirmed by four observed positive properties possessed by it, are :—

1. The spectrum of argon observed by Crookes under a low press Geissler-Plücker tubes) distinguishes it from other gases.[7] It was by this means that the argon obtained by means of magnesium is id with that which remains after the conversion of the atmospheric n into nitric acid. Like nitrogen, argon presents two spectra produ different potentials of the induced current, one being orange-red, th steel-blue; the latter is obtained under a higher degree of rarefacti with a battery of Leyden jars. Both the spectra of argon (in contradis to those of nitrogen) are distinguished by clearly defined lines.[8] T (ordinary) spectrum of argon has two particularly brilliant and charac red lines (not far from the bright red line of lithium, on the opposite the orange band) having wave-lengths 705·64 and 696·56 (*see* p. 565). Between these bright lines there are in addition lines wit lengths 603·8, 565·1, 561·0, 555·7, 518·58, 516·5, 450·95, 420·10, 415 394·85. Altogether 80 lines have been observed in this spectrum and the blue spectrum, of which 26 are common to both spectra.[9]

2. According to Rayleigh and Ramsay the solubility of argon i is approximately 4 volumes in 100 volumes of water at 13°. Thus is nearly $2\frac{1}{2}$ times more soluble than nitrogen, and its solubil proaches that of oxygen. Direct experiment proves that nitrogen o from air from boiled water is heavier than that obtained straight fr atmosphere. This again is an indirect proof of the presence of ar air.

3. The ratio k of the two specific heats (at a constant pressure

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[7] The greatest brilliancy of the spectrum of argon is obtained at a tension o while for nitrogen it is about 75 mm. (Crookes). In Chapter V., Note 16 bis, i that the same blue line observed in the spectrum of argon is also observed in the of nitrogen. This is a mistake, since there is no coincidence between the blue the argon and nitrogen spectra. However, we may add that for nitrogen the f moderately bright lines are known of wave-lengths 585, 574, 544, 516, 457, 442, 436, which are repeated in the spectra (red and blue) of argon, judging by researches (1895); but it is naturally impossible to assert that there is perfect until some special comparative work has been done in this subject, which is very d and more especially for the bluish-violet portion of the spectrum, more par between the lines 442–436, as these lines are distinguished by their brilliancy in argon and nitrogen spectra. The above-mentioned supposition of argon being poly nitrogen (N_3), formed from nitrogen (N_2), with the evolution of heat, might fi support should it be found after careful comparison that even a limited nu spectral lines coincided.

[8] At first the spectrum of argon exhibits the nitrogen lines, but after a cert these lines disappear (under the influence of the platinum, and also of Al and with the latter the spectrum of hydrogen appears) and leave a pure argon spect does not appear clear to me whether a polymerisation here takes place or absorption. Perhaps the elucidation of this question would prove importan history of argon. It would be desirable to know, for instance, whether the vo argon changes when it is first subjected to the action of the electric discharge.

[9] Crookes supposes that argon contains a mixture of two gases, but as he reasons for this, beyond certain peculiarities of a spectroscopic character, we

a constant volume) of argon was determined by Rayleigh and Ramsay by the method of the velocity of sound (*see* Chapter XIV., Note 7 and Chapter VII., Note 26) and was found to be nearly 1·66, that is greater than for those gases whose molecules contain two atoms (for instance, CO, H_2, N_2, air, &c., for which k is nearly 1·4) or those whose molecules contain three atoms (for instance, CO_2, N_2O, &c., for which k is about 1·3), but closely approximate to the ratio of the specific heats of mercury vapour (Kundt and Warburg, $k = 1·67$). And as the molecule of mercury vapour contains one atom, so it may be said that argon is a simple gaseous body whose molecule contains one atom.[10] A compound body should give a smaller ratio. The experiments upon the liquefaction of argon, which we shall presently describe, speak against the supposition that argon is a mixture of two gases. The importance of the results in question makes one wish that the determinations of the ratio of the specific heats (and other physical properties) might be confirmed with all possible accuracy.[11] If we admit, as we are obliged to do for the present, that argon is a new element, its density shows that its atomic weight must be nearly 40, that is, near to that of K = 39 and Ca = 40, which does not correspond to the existing data respecting the periodicity of the properties of the elements in dependence upon their atomic weights, for there reason on the basis of existing data for admitting any intermediate el between Cl = 35·5 and K = 39, and all the positions above potassium periodic system are occupied. This renders it very desirable that the v of sound in argon should be re-determined.[12]

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[10] This portion of Rayleigh and Ramsay's researches deserves particular attention as, so far, no gaseous substance is known whose molecule contains but one atom. Were it not for the above determinations, it might be thought that argon, having a density 20, has a complex molecule, and may be a compound or polymerised body, for instance, N_3 or NX_n, or in general X_n; but as the matter stands, it can only be said that either (1) argon is a new, peculiar, and quite unusual elementary substance, since there is no reason for assuming it to contain two simple gases, or (2) the magnitude, k (the ratio of the specific heats) does not only depend upon the number of atoms contained in the molecules, but also upon the store of internal energy (internal motion of the atoms in the molecule). Should the latter be admitted, it would follow that the molecules of very active gaseous elements would correspond to a smaller k than those of other gases having an equal number of atoms in their molecule. Such a gas is chlorine, for which $k = 1·33$ (Chapter XIV., Note 7). For gases having a small chemical energy, on the contrary, a larger magnitude would be expected for k. I think these questions might be partially settled by determining k for ozone (O_3) and sulphur (S_6) (at about 500°). In other words, I would suggest, though only provisionally, that the magnitude, $k = 1·6$, obtained for argon might prove to agree with the hypothesis that argon is N_3, formed from N_2 with the evolution of heat or loss of energy. Here argon gives rise to questions of primary importance, and it is to be hoped that further research will throw some light upon them. In making these remarks, I only wish to clear the road for further progress in the study of argon, and of the questions depending on it. I may also remark that if argon is N_3 formed with the evolution of heat, its conversion into nitrogen, N_2, and into nitride compounds (for instance, boron nitride or nitride of titanium) might only take place at a very high temperature.

[11] Without having the slightest reason for doubting the accuracy of Rayleigh and Ramsay's determinations, I think it necessary to say that as yet (February 1895) I am only acquainted with the short memoir of the above chemists in the 'Proceedings of the Royal Society,' which does not give any description of the methods employed and results obtained, while at the end (in the general conclusions) the authors themselves express some doubt as to the simple nature of argon. Moreover, it seems to me that (Note 10) there must be a dependence of k upon the chemical energy. Besides which, it is not clear what density of the gas Rayleigh and Ramsay took in determining k. (It seems

4. Argon was liquefied by Professor Olszowsky, who is well known classical researches upon liquefied gases. These researches have an e interest since they show that argon exhibits a perfect constancy

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[12] If it should be found that k for argon is less than 1·4, or that k is depende the chemical energy, it would be possible to admit that the molecule of argon not one, but several atoms—for instance, either N_3 (then the density would be 2 is near to the observed density) or X_6, if X stand for an element with an atomic near to 6·7. No elements are known between H = 1 and Li = 7, but perhaps t exist. The hypothesis A = 40 does not admit argon into the periodic system. molecule of argon be taken as A_2—*i.e.* the atomic weight as A = 20—argon ap finds a place in Group VIII., between F = 19 and Na = 23; but such a position co be justified by the consideration that elements of small atomic weight belon category of typical elements which offer many peculiarities in their properti seen on comparing N with the other elements of Group V., or O with those of Gr Apart from this there appears to me to be little probability, in the light of the law, in the position of an inert substance like argon in Group VIII., between suc elements as fluorine and sodium, as the representatives of this group by their weights and also by their properties show distinct transitions from the element last groups of the uneven series to the elements of the first groups of the even ser instance,

Group	VI.	VII.	VIII.	I.	II.
	Cr	Mn	Fe,Co,Ni	Cu	Zn

While if we place argon in a similar manner,

VI.	VII.	VIII.	I.	II.
O = 16	F = 19	A = 20	Na = 23	Mg = 24

although from a numerical point of view there is a similar sequence to the ab from a chemical and physical point of view the result is quite different, as the such resemblance between the properties of O, F and Na, Mg, as between Cr, Cu, Zn. I repeat that only the typical character of the elements with smal weights can justify the atomic weight A = 20, and the placing of argon in Grou amongst the typical elements; then N, O, F, A are a series of gases.

It appears to me simpler to assume that argon contains N_3, especially as present in nitrogen and accompanies it, and, as a matter of fact, none of the properties of argon are contradictory to this hypothesis.

These observations were written by me in the beginning of February 1895 the 29th of that month I received a letter, dated February 25, from Professor informing me that 'the periodic classification entirely corresponds to its (argon's weight, and that it even gives a fresh proof of the periodic law,' judging f researches of my English friends. But in what these researches consisted, and above agreement between the atomic weight of argon and the periodic system wa at, is not referred to in the letter, and we remain in expectation of a first public the work of Lord Rayleigh and Professor Ramsey. [For more complete inform papers read before the Royal Society, January 31, 1895, February 13, March May 21, 1896, and a paper published in the Chemical Society's Transaction p. 684. For abstracts of these and other papers on argon and helium, and co properties in the liquid and critical states, which almost[13] disposes of the supposition that it contains a mixture of two or more unknown gases. As the first experiments showed, argon remains a gas under a pressure of 100 atmospheres and at a temperature of −90°; this indicated that its critical temperature was probably below this temperature, as was indeed found to be the case when the temperature was lowered to −128°.6[14] by means of liquid ethylene. At this temperature argon easily liquefies to a colourless liquid under 38 atmospheres. The meniscus begins to disappear at between

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[13] There only remains the very remote possibility that argon consists of a mixture of two gases having very nearly the same properties.

[14] The following data, given by Olszewski, supplement the data given in Chapter II., Note 29, upon liquefied gases.

	(tc)	(pc)	t	t_1	s
N_2	−146°	35	−194°.4	−214°	0.885
CO	−139°.5	35.5	−190°	−207	?
A	−121°	50.6	−187°	−189°.6	1.5
O_2	−118°.8	50.8	−182°.7	?	1.124
NO	−93°.5	71.2	−153°.6	−167	?
CH_4	−81°.8	54.9	−164°	−185°.8	0.415

where tc is the absolute (critical) boiling point, pc the pressure (critical) in atmospheres corresponding to it, t the boiling point (under a pressure of 760 mm.), t_1 the melting point, and s the specific gravity in a liquid state at t.

The above shows that argon in its properties in a liquid state stands near to oxygen (as it also does in its solubility), but that all the temperatures relating to it (tc, t, and t_1) are higher than for nitrogen. This fully answers, not only to the higher density of argon, but also to the hypothesis that it contains N_3. And as the boiling point of argon differs from that of nitrogen and oxygen by less than 10°, and its amount is small, it is easy to understand how Dewar (1894), who tried to separate it from liquid air and nitrogen by fractional distillation, was unable to do so. The first and last portions were identical, and nitrogen from air showed no difference in its liquefaction from that obtained from its compounds, or from that which had been passed through a tube containing incandescent magnesium. Still, it is not quite clear why both kinds of nitrogen, after being passed over the magnesium in Dewar's experiments, exhibited an almost similar alteration in their properties, independent of the appearance of a small quantity of hydrogen in them.

Concluding Remarks (March 31, 1895). The 'Comptes rendus' of the Paris Academy of Sciences of March 18, 1895, contains a memoir by Berthelot upon the reaction of argon with the vapour of benzene under the action of a silent discharge. In his experiments, Berthelot succeeded in treating 83 per cent. of the argon taken for the purpose, and supplied to him by Ramsay (37 c.c. in all). The composition of the product could not be determined owing to the small amount obtained, but in its outward appearance it quite resembled the product formed under similar conditions by nitrogen. This observation of the famous French chemist to some extent supports the supposition that argon is a polymerised variety of nitrogen whose molecule contains N_3, while ordinary nitrogen contains N_2. Should this supposition be eventually verified, the interest in argon will not only not lessen, but become greater. For this, however, we must wait for further observations and detailed experimental data from Rayleigh and Ramsay.

The latest information obtained by me from London is that Professor Ramsay, by treating cleveite (containing PbO, UO_3, Y_2O_3, &c.) with sulphuric acid, obtained argon, and, judging by the spectrum, helium also. The accumulation of similar data may, after detailed and diversified research, considerably increase the stock of chemical knowledge which, constantly widening, cannot be exhaustively treated in these 'Principles of Chemistry,' although very probably furnishing fresh proof of the 'periodicity of the

− 119°·8 and − 121°·6, mean − 121° at a pressure of 50·6 atmospheres. vapour tension of liquid argon at − 128°·6, is 38·0 atmospheres, at − it is one atmosphere, and at − 189°·6 it solidifies to a colourless subst like ice. The specific gravity of liquid argon at about − 187° is nearl which is far above that of other liquefied gases of very low absolute bo point.

The discovery of argon is one of the most remarkable chemical acc tions of recent times, and we trust that Lord Rayleigh and Professor Ran who made this wonderful discovery, will further elucidate the true natu argon, as this should widen the fundamental principles of chemistry, to v the chemists of Great Britain have from early times made such val contributions. It would be premature now to give any definite opi upon so new a subject. Only one thing can be said; argon is so inert its *rôle* in nature cannot be considerable, notwithstanding its presence i atmosphere. But as the atmosphere itself plays such a vast part i life of the surface of the earth, every addition to our knowledge of its co sition must directly or indirectly react upon the sum total of our know of nature.

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